U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-280 058

Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors: Supporting Documentation

Environmental Protection Agency, Research Triangle Park, N.C.

Feb 78

PB 280 058

EPA-450/2-77-021b

February 1978

PROCEDURES FOR QUANTIFYING RELATIONSHIPS BETWEEN PHOTOCHEMICAL OXIDANTS AND PRECURSORS: SUPPORTING DOCUMENTATION

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

U.S. ENVIRONMENTAL PROTECTION AGENCY
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/2-77-021b	2.
3. RECIPIENT'S ACCESSION NO. PB280058	
4. TITLE AND SUBTITLE Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors: Supporting Documentation	5. REPORT DATE February 1978
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W.P. Freas, E.L. Martinez, E.L. Meyer, N.C. Possiel, D.H. Sennett and J.E. Summerhays	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Monitoring and Data Analysis Division Research Triangle Park, N.C. 27711	10. PROGRAM ELEMENT NO. 2AA635
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as Box 9	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This report is a companion document to EPA-450/2-77-021a, Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. Particular emphasis is placed on providing additional background documentation on the development of the Empirical Kinetic Modeling Approach (EKMA). Specifically, the report describes: (1) procedures for estimating the prevailing 6-9 a.m. NMHC/NO_x ratio for a city, (2) the use of default NMHC/NO_x ratios, (3) procedures for estimating transported ozone concentrations and (4) the results of kinetic model simulations for a range of meteorological conditions and precursor levels. Topics which have general significance in a number of different procedures for quantifying ozone-precursor relationships include the prevailing background concentration of ozone and the greater importance of transported ozone as opposed to transported precursors.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Ozone Hydrocarbons Nitrogen Oxides Meteorology Transport Kinetic Models	EKMA Isopleths	

18. DISTRIBUTION STATEMENT Release unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 109
	20. SECURITY CLASS (This page) Unclassified	22. PRICE A06-A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/2-77-021b

PROCEDURES FOR QUANTIFYING RELATIONSHIPS BETWEEN PHOTOCHEMICAL OXIDANTS AND PRECURSORS: SUPPORTING DOCUMENTATION

February 1978

Monitoring and Data Analysis Division

Office of Air Quality Planning and Standards

Research Triangle Park, North Carolina 27711

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This document has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication. Subject to clarification, the contents reflect current Agency thinking.

Table of Contents

	Page
List of Figures	iv
List of Tables	v
Executive Summary	vii
1.0 Introduction	1-1
2.0 Natural Background Concentrations of Ozone and Precursors and Their Resulting Impact on Urban Ozone Levels	2-1
2.1 Introduction	2-1
2.1.1 Purpose	2-1
2.1.2 Background	2-1
2.2 Natural Ozone in Rural Areas	2-3
2.2.1 Stratospheric Source	2-4
2.2.1.1 Effect of Slow Transfer/Diffusion Process	2-6
2.2.1.2 Effect of Stratospheric Intrusions	2-6
2.2.2 Natural Sources of Precursors	2-8
2.2.3 Estimated Impact of Natural (Vegetative) Precursor Sources	2-9
2.3 Estimated Impact of the Transport of Natural Background Concentrations into Urban Areas	2-12
2.4 Summary and Conclusions	2-13
2.5 References	2-17
3.0 Estimating NMHC/NO_x Ratios for Use in the Empirical Kinetic Modeling Approach (EKMA)	3-1
3.1 Introduction	3-1
3.1.1 Purpose	3-1
3.1.2 Background	3-1
3.2 NMHC/NO_x Ratios for Use in EKMA	3-4

Table of Contents (cont'd)

		Page
3.2.1	Spatial Variation in NMHC/NO_x Ratios	3-6
3.2.2	Uncertainty in Individual NMHC Readings	3-9
3.2.3	Diurnal and Spatial Variation in NMHC and NOx Concentrations	3-11
3.2.4	NMHC/NO_x Ratios on High Ozone Days	3-14
3.2.5	Default NMHC/NO_x Ratios	3-16
3.3	Summary and Recommendations	3-21
3.4	References	3-25
4.0	Variation of Ozone and Precursor Levels in and Near Urban Areas	4-1
4.1	Introduction	4-1
4.1.1	Purpose	4-1
4.1.2	Background	4-1
4.2	Ozone Concentrations Measured Upwind of Urban Areas	4-2
4.3	Urban Precursor Variations	4-4
4.4	Summary	4-8
4.5	References	4-12
5.0	The Impact of Inter-Urban Pollutant Transport on Oxidant Concentrations	5-1
5.1	Introduction	5-1
5.2	The Simulation Model	5-2
5.3	Conditions Simulated	5-2
5.4	The Impact of Transport of Various Pollutants on Ozone Concentrations	5-6
5.5	The Impact of Ozone Transport under Various Conditions	5-17
5.6	Anticipated Trends in the Impact of Ozone Transport	5-28

Table of Contents (cont'd)

		Page
5.7	Conclusions	5-32
5.8	References	5-35
6.0	Acknowledgements	6-1

List of Figures

		Page
2.1	Scavenging - mixing - dilution of natural O_3 component in vicinity of an urban area.	2-14
3.1	Sensitivity of maximum afternoon ozone concentrations to morning precursor levels measured upwind.	3-3
3.2	RAPS monitoring network and surrounding urban areas.	3-5
3.3	Histograms of 6-9 a.m. NMHC/NO_x ratios at selected RAPS sites.	3-10
3.4	Average diurnal variation in NMHC (St. Louis RAPS, June-October 1976).	3-12
3.5	Average diurnal variation in NO_x (St. Louis RAPS, June-October 1976).	3-13
3.6	Sensitivity of maximum afternoon ozone concentrations to precursor concentrations, given default NMHC/NO_x ratios.	3-20
4.1	Ozone monitoring sites around the Philadelphia-Camden metropolitan area.	4-5
4.2	Variation of 6-9 a.m. average NMHC with distance from Site 101 (June-October 1976).	4-9
4.3	Variation of 6-9 a.m. average NO_x with distance from Site 101 (June-October 1976).	4-10
5.1	Role of ozone aloft on maximum surface ozone levels: a conceptual view.	5-8
5.2	Primary set of simulated conditions.	5-20
5.3	Additional conditions simulated.	5-21

List of Tables

		Page
2.1	Typical Estimates of Natural Contribution to Ambient Ozone Levels During the Photochemical Oxidant Season.	2-7
3.1	Ambient Data from Urban and Suburban Sites Used to Estimate Default Ratios.	3-7
3.2	Example of Sensitivity of Suburban Ambient Data to Wind Direction -- Portland, Maine.	3-8
3.3	Comparison of NMHC/NO_x Ratios for Selected Sites in St. Louis, 1976.	3-15
3.4	Comparison of NMHC/NO_x Ratios on High Ozone Days for Selected Cities.	3-17
3.5	Comparison of Concentrations of NMHC and NO_x on High Ozone Days with Seasonal Mean Concentrations at RAPS Sites.	3-18
4.1	Upwind Ozone Concentrations for Selected Cities on High Ozone Days During 1975.	4-3
4.2	Ozone Concentrations Measured Upwind of St. Louis on Nine High Ozone Days in 1976.	4-6
4.3	Significance of Transported Precursor Concentrations.	4-7
5.1	Base Set of Conditions Assumed in Kinetics Model Simulations.	5-3
5.2	Conditions Assumed in Simulating the Transport of Various Pollutants.	5-11
5.3A	The Impact of Worst Case Transport of Various Pollutants on Peak Ozone Concentrations.	5-15
5.3B	The Impact of Typical Case Transport of Various Pollutants on Peak Ozone Concentrations.	5-16
5.4	The Impact of Ozone Transport in Different Atmospheric Layers.	5-18
5.5	Impact of Ozone Transported Aloft.	5-23
5.6	Impact of Ozone Transported Aloft Under Different Emission Conditions.	5-26
5.7	Impact of Ozone Transported Aloft Under Different Insolation Assumptions.	5-27

List of Tables (cont'd)

		Page
5.8	The Impact of Ozone Transport Under Varying Conditions -- Summary of Results.	5-29
5.9	The Impact of Ozone Transport as Air Quality Approaches the NAAQS.	5-31

Executive Summary

The purpose of this report is to provide more extensive documentation for many of the assertions made in EPA 450/2-77-021a, Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. Several of the assertions are applicable only to the Empirical Kinetic Modeling Approach (EKMA) described at length in that document. Others, such as the prevailing background concentration of ozone and the greater importance of transported ozone as opposed to transported precursors, have general significance in a number of different procedures for quantifying ozone-precursor relationships. Specifically, eight issues are addressed:

1. What levels of ambient ozone and precursors are attributable to natural sources?

2. How significant are natural sources of ozone and precursors likely to be in contributing to maximum ozone concentrations observed within and downwind of urban areas?

3. What are typical ratios of non-methane hydrocarbon (NMHC) to oxides of nitrogen (NO_x) in urban and suburban areas?

4. How do ambient precursor concentrations vary, both spatially and diurnally, in and near urban areas?

5. Is there any apparent difference in precursor levels and NMHC/NO_x ratios on days experiencing high ozone concentrations as opposed to other days?

6. Can existing ambient data be used to draw inferences about ozone gradients upwind and downwind of major cities?

7. What is the relative importance of transported ozone, NMHC, NO_x, NO_2/NO_x ratio and aldehydes in contributing to maximum ozone concentrations observed in the vicinity of urban areas?

8. How is the impact of transported ozone likely to be affected by such factors as changes in locally generated precursor levels, prevailing NMHC/NO_x ratios, varying diurnal emission patterns, level of transported ozone aloft, prevailing atmospheric dilution rates, and sunlight intensity?

To accomplish its purpose, the report is divided into five sections. Section 1 discusses the purpose of the report and presents the format of the sections that follow.

Section 2 discusses natural background concentations of ozone and precursors and their impact on urban ozone levels. It is concluded that natural ozone in the lower troposphere primarily results from slow interchange between the stratosphere and troposphere. During the summer months, natural ozone is typically about 0.04 ppm in rural areas. As a result of scavenging by locally generated pollutants, natural sources of ozone probably do not result in more than a 0.02 ppm increase in peak ozone levels observed in urban areas.

Ambient levels of non-methane hydrocarbons measured in areas not dominated by urban plumes are quite low, in the order of 0.1 ppmC. Only a fraction of the measured NMHC in rural areas can be traced to natural sources of hydrocarbons. It should be pointed out, however, that the role played by reaction products of naturally emitted hydrocarbons in the subsequent formation of ozone is still not certain. Nevertheless, presently available information suggests that naturally emitted hydrocarbons are not significant factors in the formation of urban ozone. Ambient levels of NO_x in rural areas are frequently below the detectable limits of commercially available instrumentation. Hence, naturally emitted NO_x is not believed to be an important contributor to the urban ozone problem.

Section 3 discusses procedures for estimating NMHC/NO_x ratios for use with EKMA. Temporal and spatial variations in precursor concentrations

are also presented. Both NMHC and NO_x exhibit pronounced diurnal patterns in urban areas, with high, or near peak, concentrations occurring in the early morning (about 6-9 a.m.). Ambient precursor concentrations are lower in suburban areas, and are lower still in rural areas. Diurnal patterns in ambient precursors become less pronounced with increasing distance from a city. Measured 6-9 a.m. NMHC/NO_x ratios appear to be about 9.5:1 in urban areas. Suburban ratios appear to be close to this value on days when the suburban location is downwind from the city. Close agreement among sites is generally observed for 6-9 a.m. NMHC/NO_x ratios on days with high oxidant.

Differences in ozone and precursor concentrations measured upwind and downwind of urban areas are described in Section 4. Using available data, ozone gradients upwind and downwind of a city can only be determined for a limited number of cities. The problem is primarily one of not having suitable upwind data. Such measurements as do exist suggest that as a result of the transport of ozone over long distances (up to several hundred kilometers), ground level concentrations upwind from a city may be in the order of 0.05 to 0.13 ppm on days with high ozone. Since only limited data were available for the analysis, however, higher values cannot be ruled out.

In Section 5, the kinetics model underlying EKMA is used to estimate which facet of long-range transport is likely to exert the most significant impact on maximum ozone concentrations in urban areas. Simulations are also performed to determine how the impact of transported ozone on maximum urban ozone concentrations is affected by changes in local

precursors and meteorology. The results of these simulations are somewhat qualitative, since the model used assumes instantaneous, homogeneous vertical mixing of pollutants beneath the atmospheric mixing depth. If the actual time required for thorough vertical mixing is as great as or greater than the time required for chemical reactions to occur, some uncertainty is introduced.

The results of the simulations suggest that ozone transported aloft overnight (i.e., above the morning mixing height but below the afternoon mixing height) is generally the most significant facet of long-range transport. The impact of transported aldehydes were found to be insignificant. The impact of 0.1 ppmC of NMHC (believed typical of levels found in rural areas) on peak ozone concentrations was found to be quite low, in the order of 0.01 to 0.02 ppm ozone. If a monitoring site is located within an urban plume (e.g., NMHC $\sim$ 0.3 ppmC and $NO_x \sim$ 0.04 ppm), under some circumstances the impact of transported NMHC and NO_x on peak ozone concentrations may approach or violate the NAAQS for oxidant.

For the range of conditions examined, the simulations suggest that ozone transported aloft overnight may be from "20 to 70% additive." For example, if 0.10 ppm ozone were transported aloft and were "50% additive," its impact on maximum ground level ozone concentration in the urban area would be 0.05 ppm. Modeling results imply that the impact of ozone transported aloft increases: a) as local precursor levels are decreased, b) as the NMHC/NO_x ratio decreases, c) as the concentration of transported ozone increases, and d) as the atmospheric dilution rate increases. These results imply that, as local emissions decrease in future years,

the relative impact of a given transported ozone concentration vis à vis local emissions may increase. However, as control programs are implemented upwind, the transported ozone concentration can be expected to be reduced. The result is likely to be a reduced impact of transport in future years.

1.0 Introduction

In a companion report, Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors, EPA-450/2-77-021a, several methods for relating ambient oxidant (measured as ozone) to non-methane hydrocarbons and oxides of nitrogen have been described. That document discusses Eulerian and Lagrangian photochemical dispersion models, an Empirical Kinetic Modeling Approach, linear rollback and statistical approaches. Procedures for integrating long-range transport considerations into these approaches are also described. Because the EKMA approach is less well known and documented than many of the other methods, it is described in greater detail. In the companion report, the basis for a number of statements concerning the propriety of several EKMA assumptions was not fully documented. In addition, a number of assumptions concerning the behavior and prevalence of ozone and precursors are common to the other approaches as well as to EKMA. To be more specific, the following questions are implied in the previous document:

1. What is the basis for the assertions concerning natural background concentrations of ozone and precursors?
2. What levels of NMHC, NO_x and ozone appear to be transported over long distances?
3. How do urban NMHC and NO_x concentrations vary spatially and temporally? Do these variations support assumptions made in EKMA?
4. Which facet(s) of transport exerts significant impacts on the urban ozone problem, and what is the basis for the conclusions drawn about this issue?
5. To what extent is the impact of transported ozone likely to vary under differing levels of local emissions and meteorological conditions?

The purposes of this report are: 1) to document more extensively the basis for some of the assumptions which were made in the previously referenced companion document, and 2) to answer as fully as possible, given the present state of knowledge, a number of questions which may have arisen from a reading of the companion document. The report is divided into this and four additional sections. Section 2 discusses natural background levels of ozone and precursors. The results of field studies, laboratory investigations and kinetics model simulations are used to estimate the likely significance of natural background concentrations in urban areas. Section 3 discusses procedures for estimating NMHC/NO_x ratios for use with EKMA. Observed temporal and spatial distributions of NMHC and NO_x concentrations are also presented, with particular emphasis on data collected during the St. Louis Regional Air Pollution Study (RAPS). Section 4 discusses differences in ozone and precursor concentrations observed upwind and downwind of several large cities. Section 5 describes the results of mathematical simulations which have been obtained using the chemical kinetics model underlying EKMA. These simulations are used to estimate the impact of transported ozone, NMHC, NO_x, prevailing NO_2/NO_x ratio and aldehydes on maximum ozone concentrations observed in urban areas. The degree to which the impact of transported ozone may be affected by changes in levels of locally generated precursors, NMHC/NO_x ratios, diurnal emission patterns, atmospheric dilution and sunlight intensity is also reported. These latter observations are used to suggest the importance which transported ozone may assume in future years when the National Ambient Air Quality Standard (NAAQS) for photochemical oxidants is approached in the vicinity of urban areas.

As with any photochemical model, it is difficult to verify the EKMA model because of the rarity of suitable observed data. However, model verification is essential to assure that the approach provides reasonable results.

Various EPA efforts are planned to verify EKMA. These efforts are being directed along three lines of inquiry. These include: (1) comparisons of Los Angeles ambient trend data with predictions using EKMA isopleths, (2) combining of the kinetics model underlying EKMA with observed meteorological and emissions data and comparison of the estimates with ambient air quality collected in the RAPS monitoring network, and (3) comparisons of EKMA predictions with those obtained from more complex Eulerian and Lagrangian models. Results of these efforts will be reported as they become available.

Presently, only one comparison has been completed, the results of which are described in a recent EPA report.* This effort compared the standard isopleth version of EKMA for the basin and fixed sites with historical Los Angeles ambient data. Considering the potential errors in estimating oxidant and precursor changes for this analysis, the conclusion is that the basinwide isopleth predictions "are not inconsistent with historical trends." However, comparisons made at some specific sites for fixed irradiation times have indicated that the standard isopleths tend to underestimate the oxidant level improvements in Los Angeles. The recommended procedure is to apply EKMA basinwide. Therefore, the verification results for the basinwide application are most pertinent.

---

* J. Trijonis and D. Hunsaker, Verification of the Isopleth Method for Relating Photochemical Oxidant to Precursors, EPA-600/3-78-019, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1978.

These results represent an initial review of the EKMA approach. Other verification efforts are needed and are underway. More sophisticated comparisons of EKMA are being planned with the RAPS St. Louis data and in other urban areas where a large data base exists. As previously mentioned, the results of these verification studies will be reported as they become available.

2.0 Natural Background Concentrations of Ozone and Precursors and Their Resulting Impact on Urban Ozone Levels

2.1 Introduction

2.1.1 Purpose

The purpose of this section is to explain the basis for recommending natural ozone (O_3) and naturally emitted ozone precursor concentrations that should generally be assumed to be transported into urban environments. These values may be used in the application of various procedures described in the companion document[1] for quantifying oxidant-precursor relationships. This section will describe the general circumstances for which the recommended values are applicable and will identify possible exceptions. The focus is on estimates of natural background values transported into urban areas, since modeling approaches for oxidant control plan development will largely be confined to urban areas and their environs, where oxidant problems will tend to be most severe. Transported anthropogenic ozone is considered separately (in Section 4), because, unlike natural ozone, it is likely to be more area-specific.

2.1.2 Background

The original Appendix J method[2] for estimating oxidant control requirements assumed zero background for O_3 and non-methane hydrocarbons. The method did not consider oxides of nitrogen. When the method was conceived, it was generally assumed that morning precursor emissions in the urban center were associated with high afternoon oxidant concentrations in the same central area. At that time, few oxidant or O_3 monitors existed beyond the urban centers to suggest that transport could cause maximum concentrations at significant distances downwind. The few oxidant measurements that were

available for remote areas indicated a very low rural background (~ 0.02 ppm).[3] For the urban center, it was assumed that, during the night and early morning, any ambient O_3 remaining from the preceding day would be completely scavenged principally by reactions with nitric oxide (NO). This assumption seemed to be borne out by existing surface measurements. Little evidence existed of significant influence from O_3 layers aloft or long-range horizontal transport from other areas (urban or rural). However, under the stagnant conditions generally assumed to accompany peak O_3 concentrations, transport considerations would be minimal. Therefore, on the basis of the information then available and the assumptions deemed appropriate at the time, the zero O_3 background value for urban areas was believed to be reasonable. Data on NMHC were almost nonexistent outside urban centers but were surmised to be low. Hence, a zero background was also assumed for NMHC.

More recent analyses of field data indicate that a zero background assumption for O_3 is inappropriate.[4,5,6,7,8,9] These investigations show the following:

1. In many parts of the country during the oxidant season, rural O_3 levels often violate the ambient photochemical oxidant standard. Such rural O_3 levels reflect O_3 of anthropogenic origin as well as a natural component. Measurements in remote areas indicate that the natural component is greater than previously believed, although well below the NAAQS level, except under infrequent circumstances unlikely to coincide with the season of significant photochemical oxidant formation and buildup from anthropogenic sources.

2. Maximum ozone concentrations resulting from precursor emissions in medium/large urban areas usually occur several kilometers downwind of urban centers (typically 15-30 kilometers). Even during light and variable wind conditions, maximum concentrations are not normally found in the urban centers, presumably because of the strong scavenging effect of NO emissions throughout the day.

3. During wind transport conditions, rural ozone, consisting of natural and anthropogenic components, is transported into urban areas and contributes to the maximum O_3 levels normally found downwind of the urban

centers in the afternoon. The contribution of the rural O_3 may not be entirely additive due to the scavenging effect, especially of NO upon O_3 transported into the urban area.

4. In a common air mass, the ozone concentration of the air found aloft over urban environments in the early morning tends to resemble that found near the surface in surrounding rural environments during the preceding afternoon hours. This apparently results from well developed vertical mixing during the afternoon, distributing pollutants rather uniformly over a relatively deep layer (typically 1-3 km). This uniform vertical distribution of pollutants is transported into urban areas during the night, but stability stratification separates or decouples the layer aloft from that near the surface. The surface layer undergoes rapid chemical scavenging upon entry into the urban area, while the layer aloft remains virtually unaffected. (The above description reflects a phenomenon observed with typical wind transport conditions for urban environments not directly affected by plumes from other nearby urban areas.)

5. In most urban areas, maximum O_3 concentrations occur on warm days during which the mixing height increases severalfold from morning to afternoon. For instance, three-to fivefold increases in mixing height are common in most inland locations in the eastern U.S.[10] Hence, progressive mixing with the air aloft should occur during downwind transport of the urban plume accompanied by a contribution of the O_3 mixed from aloft. The significance of the O_3 entrained from aloft is a function of the initial O_3 concentration aloft, the depletion effects of dilution during the mixing process and scavenging (principally by NO) during the morning hours.

Presently, there is still a very limited amount of precursor data available for determining levels of NO_x and NMHC advected into cities. Those data that are available are discussed in this Section and in Section 4. These data indicate that, while the incoming precursor values may not be zero, they are considerably less than concentrations resulting from precursors emitted in the urban area. In the case of NMHC, organic species data that have been collected indicate that only a small fraction of incoming NMHC is of natural (vegetative) origin.

2.2 Natural Ozone in Rural Areas

Since anthropogenic O_3 predominates in urban areas, the natural O_3 component is difficult, if not impossible, to estimate from urban measurements. Therefore, ambient measurements in rural areas are essential to

develop estimates of natural O_3 that may be transported into urban areas. Natural ambient levels of O_3, as may be reflected by measurements in more remote rural areas, are believed to result principally from two sources: (1) through interchange of air between the stratosphere and the troposphere, and (2) the synthesis of naturally emitted organic precursors (e.g., from vegetation). Other possible sources that have been mentioned are methane oxidation, lightning and surface seepage of hydrocarbons, but there is no physical evidence of appreciable ozone production from such sources.[7,8,11] Sinks for O_3 occur as a consequence of contact with surface features and of reactions with certain gases or aerosols. Surface features are considered more important as sink mechanisms in rural areas, while in urban areas, reactions with NO appear to have a greater scavenging effect.

A description of the principal natural O_3 sources and impacts in rural areas is presented in the following sub-sections.

2.2.1 Stratospheric Source

A well known large reservoir of O_3 exists in the stratosphere. Stratospheric O_3 may reach concentrations of 10 ppm or more. This layer is usually found at altitudes of 20-50 km.[12] Formation of ozone within the stratosphere occurs by reactions of ultraviolet light and oxygen. A usually abrupt increase in atmospheric stability at the boundary of the stratosphere and troposphere, termed the tropopause, normally prevents large quantities of ozone from descending into the troposphere. However, by various mechanisms which are not very well understood, there is some interchange between the layers. Much of the O_3 descending into the upper troposphere eventually reaches the lower troposphere (or biosphere) as a result of slow diffusion

and turbulent mixing processes. Dilution during downward transfer considerably reduces the high concentrations sometimes found in the vicinity of the tropopause.

Aside from the usual slow downward transfer of O_3 from the stratosphere, there is superimposed a meridional, seasonal circulation. During winter in polar regions, where the tropopause slopes toward lower elevations, relatively large quantities of O_3 are transferred downward through the tropopause. The relatively low altitude of the tropopause and frequent stormy conditions in the polar winter make it easier for O_3 to penetrate downward through the tropopause as a result of turbulent mixing. This O_3 gradually drifts southward with the weather systems, reaching an early spring maximum at mid-latitudes. Later, during the oxidant season, this meridional O_3 transport decreases, reaching a seasonal minimum during the fall.[12] During early spring months, the maximum hourly values at remote sites may approach the NAAQS. However, during the oxidant season, the stratospheric contribution to ambient O_3 levels is normally well below the level of the NAAQS.

Occasionally, intense tropospheric weather phenomena (e.g., thunderstorms, jet streams, fronts) may cause turbulent, rapid "intrusions" into the lower troposphere of unusually large quantities of ozone.[13] Ozone in these intrusions may reach the surface in only a slightly diluted form. However, such intrusions are sporadic, rare events. Also, the meteorological conditions that accompany these acute intrusions are not generally conducive to ozone formation and buildup from anthropogenic sources.[9]

There are presently no well accepted physical models for stratospheric-

tropospheric ozone exchange that can account for the tropospheric ozone burden. However, most experts tend to agree that the stratosphere is the origin of the major portion of the natural ambient O_3.

2.2.1.1 Effect of Slow Transfer/Diffusion Process

Numerous studies of O_3 measured by various means have been used to estimate the stratospheric O_3 contribution to natural O_3 background, particularly during the photochemical oxidant season. Techniques used to make such estimates include O_3 measurements in remote areas not likely to be influenced by vegetation (e.g., over oceans),[4,7] analysis of ozonesonde balloon measurements made during the 1960's,[8] and use of radioactive fallout data to assess the degree of interchange between the stratosphere and the earth's surface.[8] In addition, some investigators have measured vertical profiles of O_3 in clean air above a low subsidence inversion and have extrapolated those profiles to the surface.[9] All of these measurements indicate that typical or usual O_3 levels are attributed to slow transfer/diffusion processes, rather than intrusions. Results from these studies, as well as measurements made in remote land locations, are summarized in Table 2.1. A range for stratospheric contribution from 0.02 to 0.05 ppm is indicated as typical except for strong surface scavenging accompanying nocturnally formed, low-level stable layers. The estimates generally apply to the photochemical oxidant season.

2.2.1.2 Effect of Stratospheric Intrusions

It has been demonstrated by numerous studies, including those reviewed by Reiter[8] and by Davis, et al.,[13] that intrusions of stratospheric air introducing unusually large concentrations of O_3 into the troposphere are

TABLE 2.1 Typical Estimates of Natural Contribution to Ambient Ozone Levels During the Photochemical Oxidant Season*

PRINCIPAL INVESTIGATORS	LOCATIONS	ESTIMATED SOURCE CONTRIBUTION (ppm) Stratospheric	Biospheric	Total
. RASMUSSEN, et al.[14] (Washington State University)	(1) Whiteface Mt., N.Y.			.02** - .05
	(2) Elkton, Mo.			.02** - .05/06
	(3) Off U.S. West Coast	.03 - .05		.03 - .05
	(4) Buck Mt., Ore.			.01** - .04
. RIPPERTON, et al.[6] (Research Triangle Institute)	(1) Wolf Pt., Mont.			.01** - .06
	(2) Cent. Gulf Coast	≤.04		
. BLUMENTHAL, et al.[7]	Above S. Cal. Inversion	≤.04		
. REITER[8] (Colorado State University)	1960's U.S. Ozonesonde Measurements <6000' MSL	.03 - .04		
CONSENSUS		.02 - .05	<.01	.01** - .06

* Occasional levels above .08 ppm (NAAQS) have been observed, but with vigorous atmospheric mixing conditions not characteristic of manmade pollution episodes.

** Lower values of range may reflect nighttime scavenging at or near surface.

caused by penetration of the tropopause by strong jet streams, deep frontal systems and thunderstorm cell tops. These weather phenomena are most prominent during the late winter and early spring months. Ozone measurements at rural sites that seem to be associated with intrusions have exceeded 0.15 ppm[11] for periods of from a few minutes to an hour or more. However, these have been rarely observed, and the spatial extent of impact at the surface is believed to be very limited, a few kilometers at most.

For urban oxidant control strategy planning, intrusion events can usually be disregarded. Occasionally, peak observed ozone levels in the data base may be identified with an intrusion. Such data (like that of other sporadic, natural events that may cause natural pollutant contribution to be temporarily high, i.e., dust storms and forest fires for particulate matter), should not be used in strategy development.

2.2.2 Natural Sources of Precursors

Nationwide estimates of total natural NMHC and other organic emissions, mainly from vegetation, are rough approximations. Nevertheless, the available estimates are consistent in indicating that global natural emissions are several times greater than manmade emissions.[14,15] This does not necessarily imply that the emission densities or ambient concentrations of natural hydrocarbons will be high. Because natural emissions are spread over large areas, emission densities are low. In the vicinity of populated areas, emission densities of manmade sources may be considerably greater than those of natural sources. For example, an estimation for St. Louis indicates vegetative emissions may account for only about five percent of the total hydrocarbon emission burden from all sources within the metropolitan area.[16]

Vegetation emits some hydrocarbons, such as isoprene and various terpenes, which are known to be highly reactive. However, in rural areas, which tend to have extremely low, often undetectable, NO_x concentrations, these natural hydrocarbons may have more of a tendency to serve as a sink for O_3 by reacting with it to form aerosols. Recent smog chamber experiments tend to substantiate this point.[17,22] One question that remains largely unresolved is how natural organic emissions may react in and near urban areas (or other areas with substantial NO_x). Some smog chamber experiments suggest that, in the presence of NO_x, reactive hydrocarbon compounds emitted from vegetation (i.e., terpenes and isoprene) are capable of forming O_3.[18] However, atmospheric concentrations of these natural compounds in urban areas appear to be very low and are frequently undetectable.[17] A reasonable hypothesis is that these reactive hydrocarbons have already reacted with O_3 to form aerosols, or have been removed by other means, and hence are not present in urban areas to form additional ozone.

Some natural NO_x can result from biological action in soils, but NO_2 levels in ambient air in remote areas are usually below the detectable limit (0.005 ppm) of commercially available ambient measurement techniques. Thus, the natural NO_x contribution to ozone production is largely unknown, but is believed to be insignificant. Hourly levels of NO_2 reported for some eastern U.S. rural areas have infrequently ranged up to about 0.05 ppm, but such high rural levels may reflect the occasional effect of transport from urban sources.[5,6]

2.2.3 Estimated Impact of Natural (Vegetative) Precursor Sources

A number of approaches have been employed to evaluate the impact of vegetative organic emissions on ambient O_3 levels. Basically, these have involved (1) direct measurements of emission rates, (2) smog chamber experiments, and (3) ambient air studies.

Natural organic emissions from vegetation over the entire land area of the U.S. are estimated on an absolute weight basis to be greater than from anthropogenic sources. But in and near urban areas, emission densities of organic emissions from vegetation will be much lower than from manmade sources. Comparative emission densities alone would indicate a low potential for natural organics to form high concentrations of O_3.

Limited smog chamber data have indicated that terpenes and some other organic species are photochemically reactive. However, field studies generally conclude that very low concentrations of these organics are found in the atmosphere, even in rural areas. In smog chamber experiments, both very low and high terpene/NO_x ratios tend to inhibit O_3 formation. Smog chamber work by Washington State University and EPA groups shows that, even at optimum terpene/NO_x ratios of about 20:1, O_3 formation was very slight relative to other classes of hydrocarbons. When typical rural terpene/NO_x ratios were tested in the chambers, very little O_3 was formed, with a great deal of the carbon present involved in aerosol production. At optimum terpene/NO_x ratios and 100 ppbC, terpene concentrations, smog chamber simulations indicate that the resulting O_3 concentrations would not exceed 5 ppb.[18]

Too little information is available from smog chamber studies to determine the effect of mixing natural hydrocarbons with urban air. Evidently, natural hydrocarbons both enhance ozone formation through photochemical reactions as well as scavenge available O_3. It is not known at present which effect may predominate in an urban atmosphere. Of course, in urban areas, vegetation is much less abundant than in rural areas. Also, as indicated previously, it is unlikely that natural hydrocarbons from rural areas can survive long enough to be an important influence on urban ozone formation.

Ambient air studies have shown that vegetative-type hydrocarbons can be detected in or near forested areas. However, the atmospheric burden of these natural hydrocarbons is generally very low (from 10 to 50 ppbC), even in close proximity to densely wooded areas. Also, they generally constitute a small portion of the measured NMHC. The mix of hydrocarbons found at a rural site in Ohio was a dilute urban mixture.[17] Data analyzed for rural sites in Florida, North Carolina, Montana, Iowa, Louisiana and Pennsylvania show early morning levels of non-methane organics typically in the range of 50-200 ppbC.[17,23] These levels are well below those observed in urbanized areas, which were typically 5-12 times higher. In the extreme case, Los Angeles ambient levels were about 31 times those observed in rural areas.[6,17,23]

Because of their relatively low densities of emission and their extremely low concentrations in ambient air, both in absolute terms and in relation to the manmade organic burden, as well as their low ozone forming potential in areas with little NO_x (i.e., rural areas), natural organics are not likely to be significant sources of natural O_3 levels. Simple modeling estimates[19] based on measured emission rates indicate that the resulting O_3 concentrations will be extremely low, because of vertical dilution effects and because of reactions with background O_3 and hydroxyl radicals. These results suggest that terpenes and other natural hydrocarbons may serve principally as a sink for O_3 in rural areas.

Ambient ozone measurements taken in remote land and ocean areas (Table 2.1) also lead to the conclusion that vegetation is a negligible source of O_3 formation. In this table, ozone concentrations measured in remote land areas (where urban tracer levels such as fluorocarbons indicate no detectable urban

influence) can be compared with those from remote ocean areas (where vegetative hydrocarbons are nonexistent). Only slight differences are evident. The contribution of natural organic emissions to ambient ozone concentrations is estimated to be less than 0.01 ppm. This leads to the general conclusion that the most significant natural source of background O_3 is the stratosphere.

2.3 Estimated Impact of the Transport of Natural Background Concentrations into Urban Areas

From the information presented in Table 2.1 and other summaries of natural source impact,[11,19,21] the consensus is that the natural ozone contribution in nonurban areas, in most cases, will range between 0.02 and 0.05 or 0.06 ppm during the season and the part of the day that maximum ozone concentrations resulting from manmade sources will tend to occur. The most likely value is estimated to be 0.04 ppm.

An estimate can be made of the impact of the natural O_3 component in the urban plume at the location and time of maximum O_3 concentration. This estimate is based on the following set of assumptions:

1. The initial surface concentration of ozone in the urban plume during the 6-9 a.m. period of maximum precursor emissions is near zero.

2. Concentrations of natural O_3 very similar to those found in surrounding nonurban areas will exist a few hundred meters above the surface in the urban area during the early morning hours. This layer is separated by an inversion layer from freshly emitted NO and other surface scavengers.

3. As downwind transport occurs and surface heating proceeds during the day, the mixing depth will increase, so that considerable mixing with the air aloft will occur. The total increase in the mixing height will vary in extent from a fraction of the initial height in a few locations to severalfold in most locations.[10]

4. Scavenging by NO during the early stages of plume transport is significant. However, downwind from the urban areas in the afternoon, it is likely to be of less importance because of lower NO emissions.

5. Relative to vertical mixing, lateral mixing with background air

at the urban plume centerline is considered negligible over the distance traveled to the location of the maximum O_3 concentration.

A scenario depicting the above assumptions is shown in Figure 2.1. Simulations of this scenario utilizing the kinetics model underlying EKMA (discussed in Section 5) indicate that, for most U.S. cities, the impact of the background component is typically about 40-50 percent of the rural value when added incrementally to the urban plume, assuming severalfold daily changes in mixing height typical of most U.S. locations. However, in a few urban situations where the mixing height increases only slightly during the day (i.e., Los Angeles), the impact will be even less. Taking the more typical conditions above, where the impact of the natural component will be about 50 percent of the transported concentration, and taking the most probable value of 0.04 ppm for natural background, yields a suggested value of 0.02 ppm for the impact of natural background on maximum O_3 concentrations observed in urban areas. As indicated in the previous discussion, a local condition may justify using a slightly different estimate.

2.4 Summary and Conclusions

Natural background levels of ambient ozone (O_3) appear to result mainly from stratospheric-tropospheric exchange processes and slow transfer into the lower troposphere. Concentrations of ambient O_3 attributed to stratospheric origin are estimated to be generally well below the NAAQS level for photochemical oxidant, particularly during the oxidant season. However, on rare occasions, more abrupt intrusions from the stratosphere can cause localized elevated O_3 levels which may violate the NAAQS. In rural areas, scavenging by surface features provides the primary sink for natural O_3. Natural organics (i.e., terpenes) and/or their aerosol products may also scavenge O_3. In urban

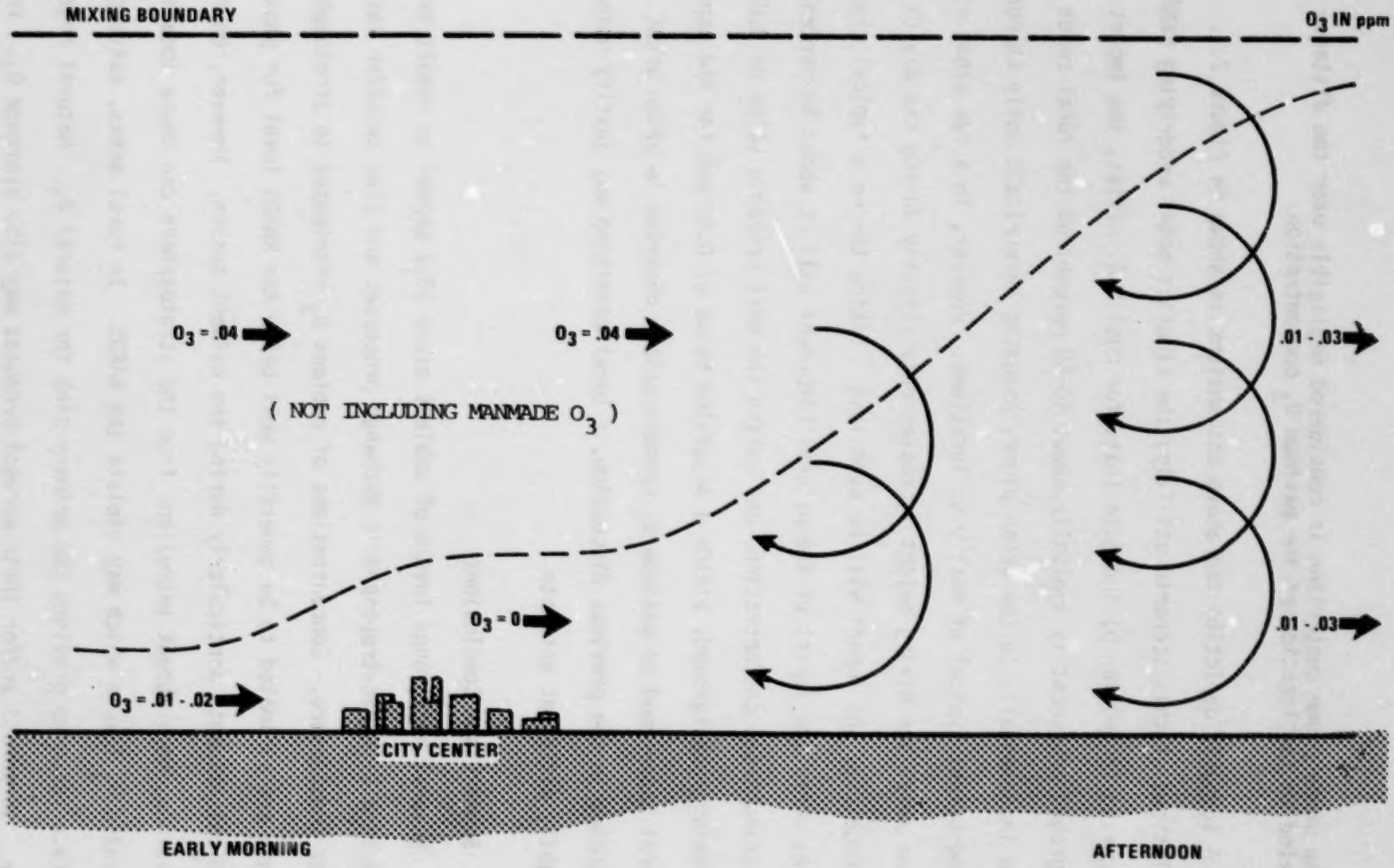

FIGURE 2.1 Scavenging-mixing-dilution of natural O_3 component in vicinity of an urban.

areas, O_3 reaction with nitric oxide (NO) emissions provides the dominant scavenging mechanism, although NO_2 produced by this scavenging reaction may at a later time regenerate O_3 through the photolytic reaction cycle.

In urban areas, early morning O_3 concentrations near the surface tend to approach zero. This results from the usual nighttime stratification of the lower atmosphere which allows efficient scavenging of the available O_3 by NO and surface features within a confined surface-based layer. However, a reservoir of O_3 remains aloft and insulated from these scavengers. This O_3 reservoir consists of natural O_3 and O_3 previously synthesized from anthropogenic precursors. These two components are usually considered as "transported O_3". During subsequent midday hours, the O_3 in the reservoir aloft is mixed downward into the surface-based layer. This mixing will affect the concentration of photochemical pollutants in the surface layer and will cause an increase in the afternoon maximum O_3 concentration observed in the vicinity of the urban area. The impact of transported pollutants is discussed more fully in Section 5.

The consensus of existing experimental data is that, on those afternoons conducive to high photochemical activity, the most likely range of natural O_3 in rural areas is 0.02 to 0.05 or 0.06 ppm, with 0.04 ppm the most likely value to assume. Nearly all of this natural O_3 background is estimated to be of stratospheric origin. Synthesis of natural precursors, mainly of vegetative origin, is estimated to contribute a negligible increment.

The kinetics model which underlies the Empirical Kinetic Modeling Approach described in Reference 1 was applied to simulate the effect of the transport of natural background concentrations of ozone on urban ozone concentrations in the presence of mixing, dilution and photochemistry. Results indicate the

impact of transported natural ozone in urban areas is about 0.01-0.03 ppm, with 0.02 ppm being the typical value that may be assumed at the location of maximum afternoon O_3 concentration. Local pecularities in meteorological conditions, levels of locally generated precursors and other factors may, in a few circumstances, justify slight deviations from the estimated 0.02 ppm value.

The sparse data available on precursor levels in rural areas that may be transported into urban areas indicate that these concentration levels are low. Moreover, only a small fraction of these low levels, at least of NMHC, have been traced to natural sources. Typically, rural levels of non-methane hydrocarbons (NMHC) appear to range from 50 to 200 ppbC. Slightly higher values may be found in the periphery of urban areas (discussed in Section 4). Nitrogen dioxide concentrations in rural areas are often near the lower threshold for commercially available instruments. However, infrequent hourly concentrations up to about 0.05 ppm may occur in some rural areas, particularly within a reasonable range for transport from urban areas (discussed in Section 4). The precursor levels typically found in rural areas are considerably less than those typically found in urban centers. Simulations with the kinetics model in EKMA (shown in Section 5) suggest that typical rural precursor levels will generally not contribute significantly to the synthesis of high ozone levels if transported into an urban area.

2.5 References

1. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

2. "Requirements for Preparation, Adoption, and Submittal of Implementation Plans." Title 40, Code of Federal Regulations: Part 51. 36 FR 15486 (August 14, 1971).

3. Air Quality Criteria for Photochemical Oxidants. U.S. Public Health Service, Washington, D.C., March 1970.

4. E. Robinson and R. A. Rasmussen, "Identification of Natural and Anthropogenic Rural Ozone for Control Purposes." Proceedings, Ozone/Oxidants Interactions With the Total Environment Specialty Conference, Air Pollution Control Association, March 1976.

5. Investigation of Ozone and Ozone Precursor Concentrations at Nonurban Locations in the Eastern United States, EPA-450/3-74-034, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1974.

6. Investigation of Rural Levels as Related to Urban Hydrocarbon Control Strategies. EPA-450/3-75-036, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1975.

7. Formation and Transport of Oxidants Along Gulf Coast and Northern U.S. EPA-450/3-76-036, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1976.

8. E. R. Reiter, "The Role of Stratospheric Import on Tropospheric Ozone Concentrations." International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings: Volume I, EPA-600/3-77-001a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1972.

9. D. L. Blumenthal, W. H. White, R. L. Peace and T. B. Smith, Determination of the Feasibility of Long-Range Transport of Ozone and Ozone Precursors. EPA-450/3-74-061, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1974.

10. G. C. Holzworth, Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Contiguous United States. AP-101, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1972.

11. H. B. Singh, F. L. Ludwig and W. B. Johnson, Ozone in Clean Remote Atmospheres: Concentrations and Variabilities. Final Report prepared for Coordinating Research Council, Stanford Research Institute, Menlo Park, California, March 1977.

12. H. U. Dutsch, "Photochemistry of Atmospheric Ozone." Advances in Geophysics, 15, 218-322 (1971).

13. D. R. Davis and R. E. Jensen, "Low-Level Ozone and Weather Systems." EPA-600/3-77-001a, ibid.

14. E. Robinson and R. C. Robbins, Sources, Abundance and Fate of Gaseous Atmospheric Pollutants. Stanford Research Institute, Menlo Park, California, February 1958. Supplement, April 1971.

15. P. Zimmerman and R. A. Rasmussen, "Measuring Organic Emissions from Vegetation." Progress Report No. 4, EPA Contract 68-02-2071, Research Triangle Park, North Carolina, November 1976.

16. Personal communication, Thomas Lahre to E. J. Lillis. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977.

17. W. A. Lonneman, "Ozone and Hydrocarbon Measurements in Recent Oxidant Transport Studies." EPA-600/3-77-001a, ibid.

18. H. H. Westberg, The Issue of Natural Organic Emissions. EPA-600/3-77-116, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1977.

19. Personal communication, J. J. Bufalini and W. A. Lonneman to E. J. Lillis. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977.

20. R. M. Angus and E. L. Martinez, "Rural Oxidant and Oxidant Transport." Proceedings of Conference on State-of-the-Art of Assessing Transportation Related Air Quality Impacts, Special Report 167, National Research Council, Washington, D.C., October 1976.

21. C. W. Spicer, "Experimental Evidence of Long Distance Pollutant Transport." Presented at Annual Meeting, American Institute of Chemical Engineers, Houston, Texas, March 1977.

22. B. W. Gay, Jr., and R. R. Arnts. "Chemistry of Naturally Emitted Hydrocarbons." International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings: Volume II, EPA-600/3-77-001b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977.

23. W. A. Lonneman, R. J. Seila and J. J. Bufalini, "Ambient Air Hydrocarbon Concentrations in Florida." Unpublished manuscript. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

3.0 Estimating NMHC/NO_x Ratios For Use in the Empirical Kinetic Modeling Approach (EKMA)

3.1 Introduction

3.1.1 Purpose

Recommendations concerning the use of non-methane hydrocarbon to oxides of nitrogen ratios in the Empirical Kinetic Modeling Approach (EKMA) have been made in Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors.[1] The purpose of Section 3 is to present the results of analyses of existing NMHC and NO_x data used to develop recommendations on the appropriate NMHC/NO_x ratio for use in EKMA (e.g., calculation procedures such as appropriate averaging time, site selection, number of sites to be examined, etc.). This section also provides a review of temporal and spatial distributions of NMHC and NO_x in St. Louis and ambient data for estimating default NMHC/NO_x ratios. The following three issues are addressed in this Section:

1. What are typical non-methane hydrocarbon to oxides of nitrogen ratios in urban and suburban areas?
2. How are ambient NMHC and NO_x concentration data used to estimate NMHC/NO_x ratios for use in EKMA?
3. How can a city without ambient NMHC and NO_x data apply EKMA?

3.1.2 Background

EKMA uses a set of ozone isopleths which depicts maximum afternoon concentrations of ozone downwind from a city as a function of initial concentrations of NMHC and NO_x. The isopleths reflect specific assumptions about the temporal distribution of emissions, meteorological conditions, reactivity of the precursor mix and concentrations of ozone transported from upwind areas.

There are two forms of EKMA, the city-specific isopleths described in Section 5 and in Reference 1, and the Standard Isopleths shown in Figure 3.1. Use of either set of isopleths for estimating the degree of reduction in ambient precursor levels needed to attain a specified ozone level is similar. That is, they both require the ozone design value (the highest second highest hourly concentration observed in or near the city during the base period designated for control strategy development purposes) and the prevailing NMHC/NO_x ratio. Reference 1 contains a detailed discussion on monitoring requirements for determining the ozone design value. Additional guidance on determining design values is provided in References 7 and 8. Therefore, this Section focuses on the second input requirement, the NMHC/NO_x ratio. As reported in the companion document,[1] the appropriate ratio for use with EKMA is the 6-9 a.m. (LDT) NMHC/NO_x ratio observed in the urban core* on the same day as the ozone design value. Concentrations measured at this time in the urban core best reflect initial conditions prior to the onset of photochemical reactions. Thus, this ratio is considered to be consistent with the results of smog chamber experiments which describe the sensitivity of afternoon maximum ozone levels to initial concentrations of NMHC and NO_x. Further, concentrations of NMHC and NO_x are typically higher during these hours. Hence, the reliability of the monitoring data is greater.

The recommended procedure for estimating NMHC/NO_x ratios for use with EKMA was developed using ambient data on prevailing precursor levels in and near urban areas. Some sources of ambient monitoring data on NMHC and NO_x levels are SAROAD, the St. Louis Regional Air Pollution Study (RAPS) and special

---

* Urban core is defined as the central city. In large cities this may encompass areas within 3-4 km of the center of the central business district. LDT is local daylight time.

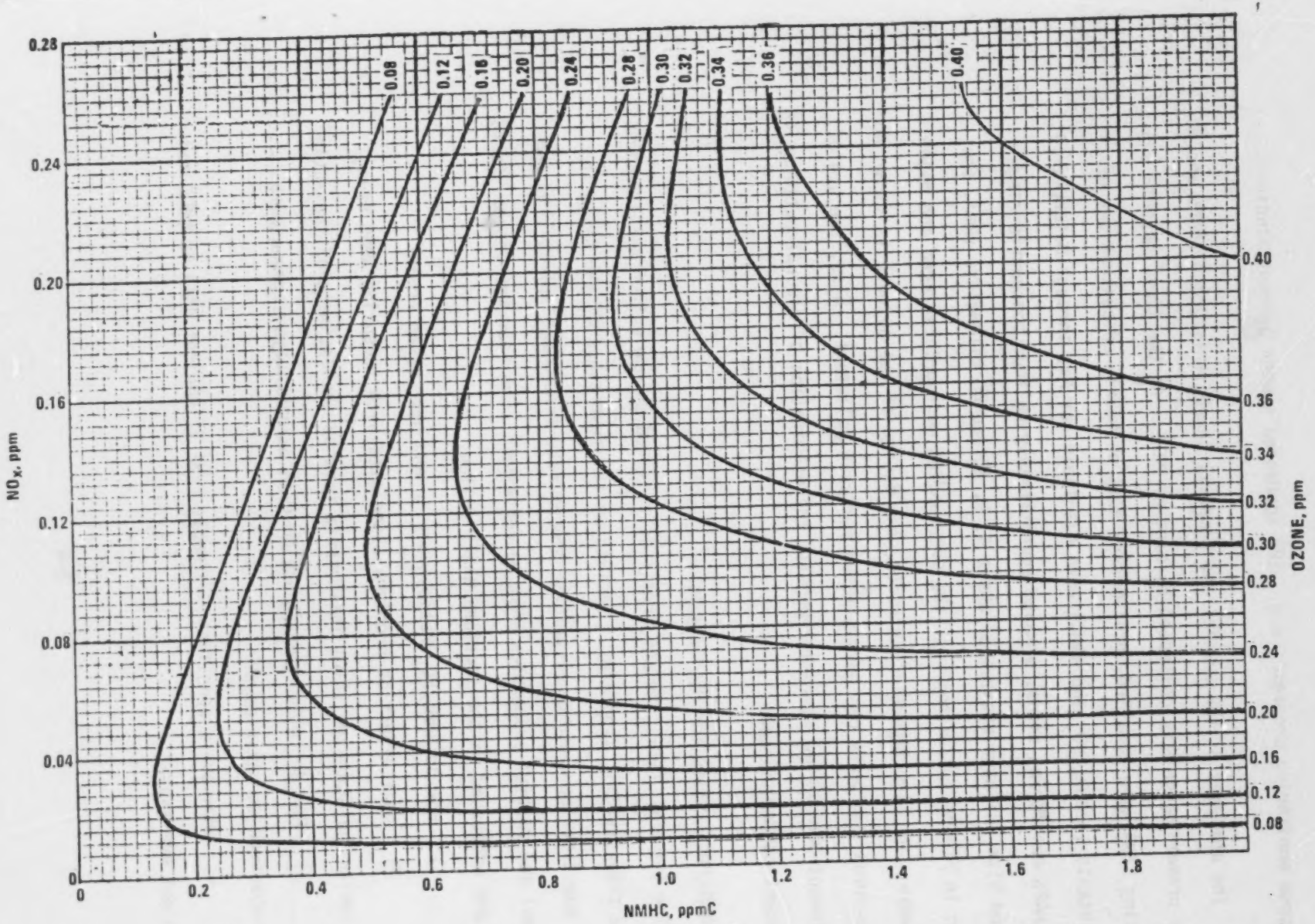

FIGURE 3.1 Sensitivity of maximum afternoon ozone concentrations to morning precursor levels measured upwind.

purpose monitoring programs (e.g., EPA sponsored summer oxidant studies).

The analyses of the spatial and temporal characteristics of NMHC and NO_x rely primarily on data collected as part of RAPS. At the time the data supporting EKMA were compiled, preliminary data on hourly concentrations of pollutants (ozone, NO_x and NMHC) were available for May through October, 1976. The RAPS monitoring sites, arrayed approximately on four concentric rings around Site 101 at distances of about 4, 9, 20 and 40 kilometers (km), are shown in Figure 3.2, along with the surrounding metropolitan area and major highways. As this figure illustrates, the design of the network is such that urban-rural gradients can be estimated for each pollutant. Also, the use of continuous monitoring equipment permits the examination of diurnal patterns in pollutant concentrations.

3.2 NMHC/NO_x Ratios For Use in EKMA

The 6-9 a.m. (LDT) NMHC/NO_x ratio is required to use either the standard or the city-specific isopleths. Because of the importance of the ratio in EKMA, questions concerning estimation procedures, instrument reliability and temporal and spatial properties must be addressed. The four key issues listed below are addressed in the sections which follow:

1) How do NMHC/NO_x ratios vary in and near urban areas?

2) What effect do problems associated with measuring NMHC using Flame Ionization Detector (FID) instruments have on the estimate of the ratio?

3) How do ratios calculated on high oxidant days compare with ratios observed on other days?

4) How can a specific city apply EKMA if ambient data on NMHC and NO_x are not available?

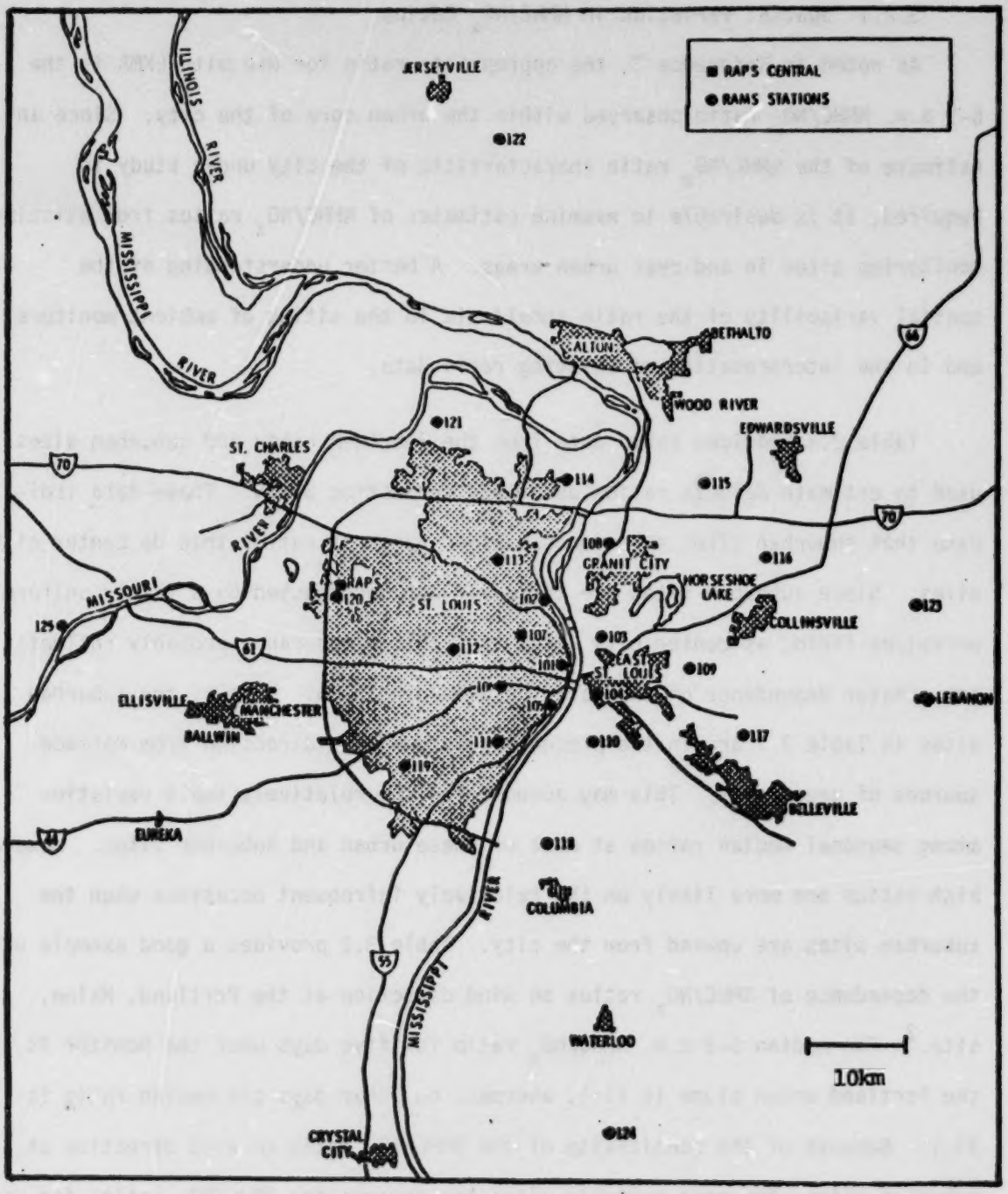

FIGURE 3.2 RAPS monitoring network and surrounding urban areas

3.2.1 Spatial Variation in NMHC/NO_x Ratios

As noted in Reference 1, the appropriate ratio for use with EKMA is the 6-9 a.m. NMHC/NO_x ratio observed within the urban core of the city. Since an estimate of the NMHC/NO_x ratio characteristic of the city under study is required, it is desirable to examine estimates of NMHC/NO_x ratios from existing monitoring sites in and near urban areas. A better understanding of the spatial variability of the ratio should aid in the siting of ambient monitors and in the interpretation of existing ratio data.

Table 3.1 provides ratio data from the fourteen urban and suburban sites used to estimate default ratios described in Section 3.2.5. These data indicate that suburban sites experience a wider range of ratios than do center city sites. Since suburban sites are typically not encompassed by a fairly uniform emissions field, as center city sites are, this wider range probably reflects the greater dependence of the ratio on wind direction. Most of the suburban sites in Table 3.1 are in the predominately downwind direction from manmade sources of precursors. This may account for the relatively small variation among seasonal median ratios at most of these urban and suburban sites. However, high ratios are more likely on the relatively infrequent occasions when the suburban sites are upwind from the city. Table 3.2 provides a good example of the dependence of NMHC/NO_x ratios on wind direction at the Portland, Maine, site.[2] The median 6-9 a.m. NMHC/NO_x ratio for five days when the monitor is in the Portland urban plume is 11:1, whereas, on other days the median ratio is 31:1. Because of the sensitivity of the NMHC/NO_x ratio to wind direction at suburban sites, the most suitable sites for determining NMHC/NO_x ratios for use in EKMA are those located in the urban core.

TABLE 3.1 Ambient Data from Urban and Suburban Sites Used to Estimate Default Ratios

(1) Site	(2) Sample Size (Days)	(3) Sampling Period	(4) Mean NMHC, ppmC (0600-0900)	(5) Mean NO_2, ppm (0600-0900)	(6) Median NMHC/NO_x Ratio (0600-0900) (Total Period)	(7) Median NMHC/NO_x Ratio on Five Highest O_3 Days (0600-0900)	(8) 90th Percentile Ratio (Total Period)	(9) 10th Percentile Ratio (Total Period)	(10) Remarks	
Austin	42	7/1-9/30/75	.27	.026	10.1:1	10.0:1	20.0:1	7.1:1	Station located 8 miles N of CBD	(S)
Corpus Christi	44	7/1-9/30/75	.65	.035	18.5:1	21.3:1	37.5:1	10.8:1	Pop = 205,000 w/many, major point sources	(U)
El Paso (Campbell St.)	35	7/1-9/30/75	.59	.067	9.3:1	9.8:1	13.2:1	4.8:1	Station 2-3 mi. S of Franklin Mtn. CBD	(U)
Houston (Mae Dr.)	39	7/1-9/30/75	1.14	.156	7.5:1	7.5:1	15.0:1	4.5:1	In heavily industrialized and populated area	(U)
Los Angeles	58	7/1-9/30/75	1.48	.147	9.8:1	10.2:1	16.8:1	6.2:1	Station located in Downtown LA	(U)
San Antonio	37	7/1-9/30/75	.22	.022	11.2:1	7.8:1	33.3:1	6.1:1	Station located 8 mi. NW of CBD	(S)
Aldine, Texas	10	7/1-9/30/75	.48	.047	11.9:1	10.0:1	40:1	7.1:1	Houston suburb, 12 mi. N of CBD and 13 mi. NW of an industrial complex	(S)
Azusa, CA	86	7/1-9/30/75	1.23	.146	8.5:1	8.0:1	15:1	5.9:1	LA suburban city (25,000), 20 mi ENE of LA CBD	(S)
Canton, OH	20	7/1-7/21/74	.56	.076	7.3:1	9.5:1	13.8:1	4.2:1	Site on Malone College Campus 2 mi. N of CBD	(S)
Dayton, OH	16	7/18-8/12/74	.59	.049	12.9:1	11.8:1	23.8:1	8.0:1	Huber Hts. site, 9 mi. NE of Dayton (pop. 243,000) CBD	(S)
El Paso (Ascarte Park)	29	7/1-9/30/75	.46	.028	10.0:1	14.0:1	40.9:1	4.0:1	In park, 6 1/2 mi. ESE from El Paso CBD and 3 mi. NE of Juarez, Mexico	(S)
Groton, CT	15	7/18-8/21/75	.24	.029	9.5:1	8.8:1	14.7:1	5.6:1	SE CT, 2 mi. S of Groton-New London (pop. 40,000)	(S)
St. Louis	150	6/1-10/31/76	.62	.077	7.6:1	8.5:1	12:1	5.8:1	Composite of 7 Stations located within 4 km of CBD	(U)
Washington, D.C.	43	7/1-8/31/76	.62	.086	7.2:1	9.2:1	13:0	3.5:1	Camp Station	(U)

(S) = suburban

TABLE 3.2 Example of Sensitivity of Suburban Ambient Data to Wind Direction -- Portland, Me.

Days When Monitor is Downwind From Portland CBD		Other Days	
Date	NMHC/NO_x	Date	NMHC/NO_x
8/7/74	7:1	7/30/74	36:1
8/19/74	17:1	7/31/74	160:1
8/21/74	6:1	8/2/74	23:1
8/22/74	11:1	8/6/74	31:1
8/23/74	14:1	8/11/74	200:1
		8/14/74	23:1
		8/24/74	26:1
Median Values	11:1		31:1

3.2.2 Uncertainty in Individual NMHC Readings

Within the past several years, there has been an increasing awareness of the problems associated with measuring ambient NMHC levels. Because NMHC is not measured directly in FID instruments but is computed from the difference between total hydrocarbons (THC) and methane (CH_4), errors in the individual values for each of these pollutants may be compounded when NMHC concentrations are calculated. This may even result in negative values for estimates of the NMHC concentration. The many operational and mechanical problems associated with FID instruments are discussed in detail elsewhere.[3]

Studies of instrument response characteristics indicate that measurement of NMHC by available commercial FID instruments yeilds unreliable individual measurements.[4] Inaccuracy in individual hourly values may be as high as $\pm$ several hundred percent in the range of concentrations below 0.5 ppmC. At higher levels, the error is considerably less, but may still be $\pm$ 25% at up to 2.0 ppmC. Because of the large potential for error that may be present in the data, use of individual NMHC measurements at a single site for one day is not recommended. Rather, if reasonable agreement is found among ratios at more than one site on the day in which the ozone design value is observed (e.g., all ratios within 50 percent of the mean ratio for all sites), the average of the individual ratios should be used as the estimate of the ratio for use with EKMA.

Figure 3.3 contrasts histograms of 6-9 a.m. NMHC/NO_x ratios calculated at RAPS Sites 101, 105, 106 and 107 with a histogram of the average ratio for these four sites. Data used in these calculations are from the period June through October, 1976. The number of observations varies from site to site because of incomplete data. For the composite of the four sites, the average ratio for a day was only computed when data for at least two of the four sites

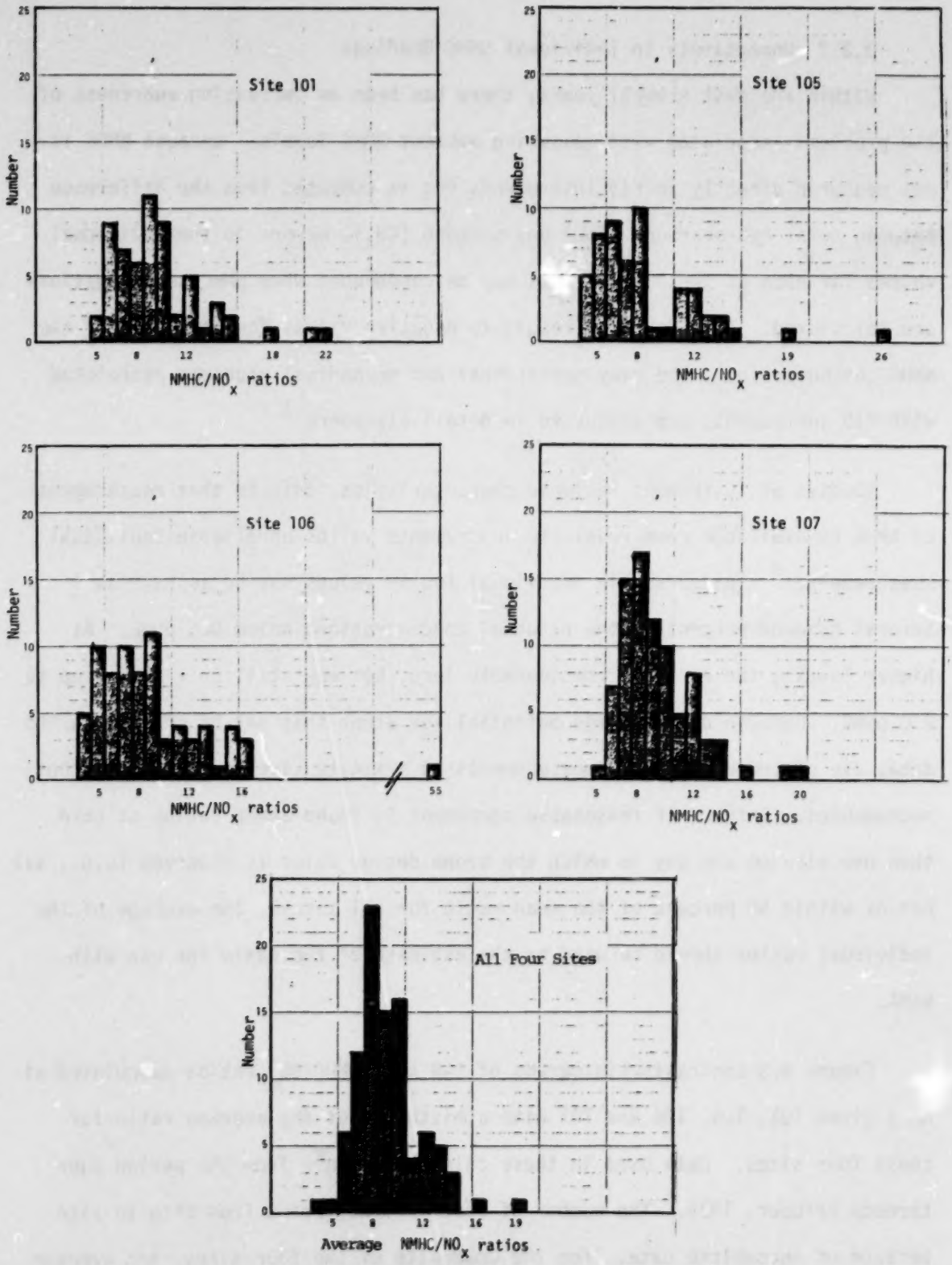

FIGURE 3.3 Histograms of 6-9 a.m. $NMHC/NO_x$ ratios at selected RAPS sites

were available. As this Figure illustrates, the averaging process tends to filter out the more extreme, and suspect, ratio values. Hence, this procedure should provide a more representative value for the prevailing ratio. For the situation when the estimated ratios among sites on a single day differ substantially, the procedure described in Section 3.2.4 is recommended.

3.2.3 Diurnal and Spatial Variation in NMHC and NO_x Concentrations

Average diurnal patterns in NMHC and NO_x concentrations at the five RAPS sites which lie approximately on a ray emanating to the north from Site 101 to Site 122 are shown in Figure 3.4 and Figure 3.5. Both NMHC and NO_x concentrations exhibit pronounced peaks during the early morning hours, then decrease rapidly to a minimum in the early afternoon before again rising during late afternoon and evening. Spatial differences among the sites are also readily apparent for both pollutants. As one proceeds outward from center city, both the absolute concentration levels and the amplitude of the diurnal curves drop off rapidly. This is particularly evident for NO_x at distant sites, where only a slight diurnal pattern is perceptible and the concentrations are, on the average, only slightly greater than the minimum detectable level of the monitoring instrument.

As noted in the previous section, the reliability of individual NMHC measurements taken with an FID instrument increases as the concentration level increases. Thus, the temporal and spatial properties of NMHC and NO_x concentrations suggest that the most reliable estimates of NMHC/NO_x ratios are those obtained at center city sites during the 6-9 a.m. period.

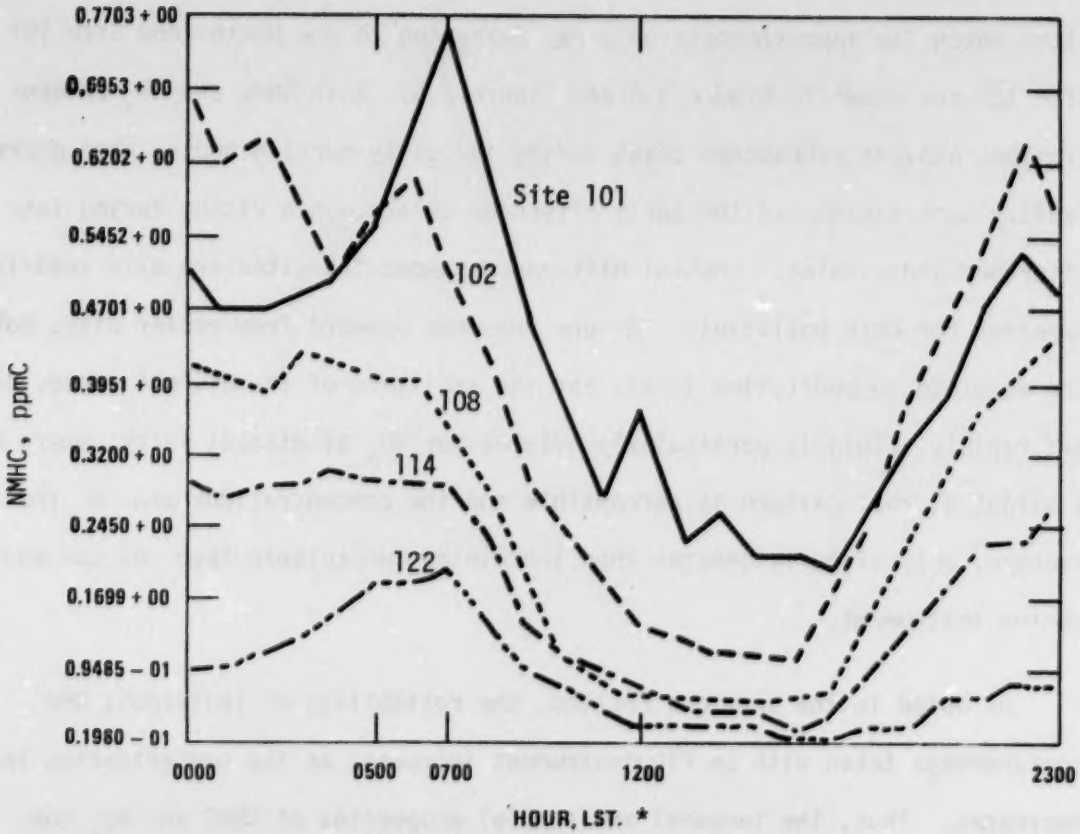

FIGURE 3.4 Average diurnal variation in NMHC (St. Louis RAPS, June-Oct. 1976)

The hour associated with RAPS pollutant data is the beginning hour in local standard time(LST),e.g. the hours denoted by 5-7 LST correspond to the 6-9 a.m. LDT period, inclusive.

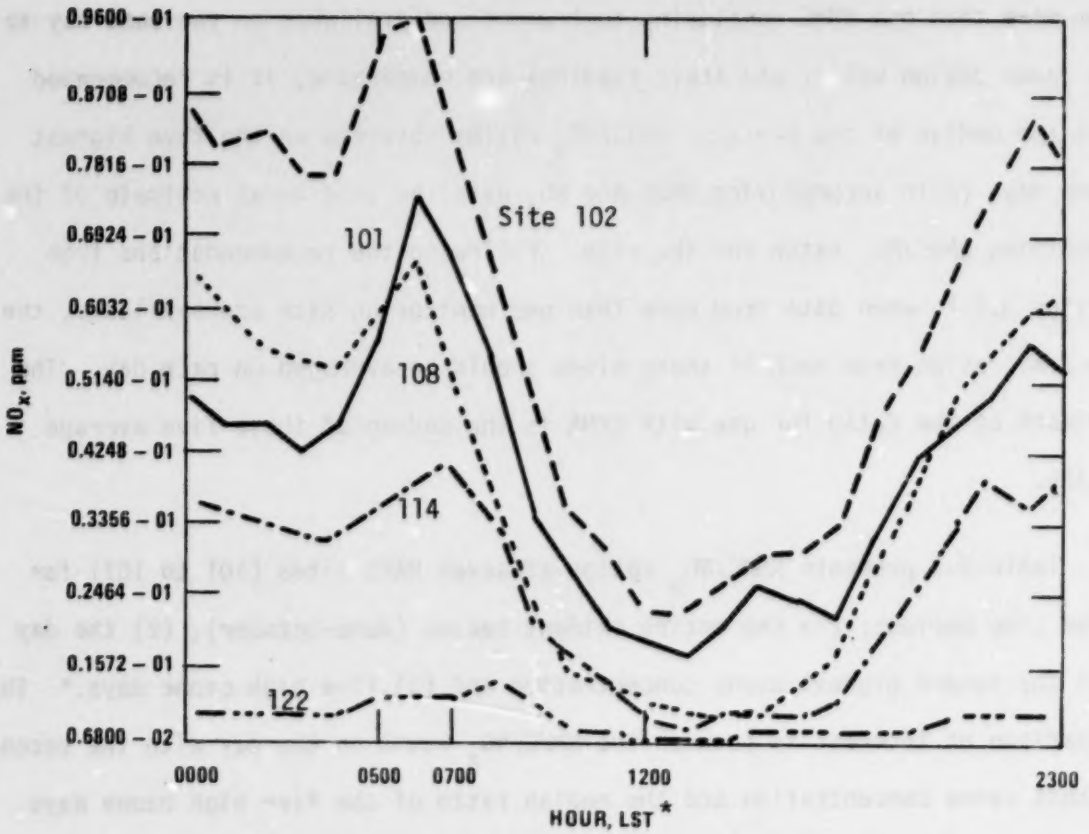

FIGURE 3.5 Average diurnal variation in NO_x (St. Louis RAPS, June-Oct. 1976)

The hour associated with RAPS pollutant data is the beginning hour in local standard time (LST), e.g. the hours denoted by 5-7 LST correspond to the 6-9 a.m. LDT period, inclusive.

3.2.4 NMHC/NO_x Ratios on High Ozone Days

Application of EKMA requires an estimate of the prevailing 6-9 a.m. NMHC/NOX ratio in the urban core on the same day as the ozone concentration used for control strategy development. Because of the concern about the accuracy of individual NMHC concentrations measured with FID instruments, an alternative procedure for estimating the ratio is suggested. Unless readings from more than one NMHC monitoring instrument are available on the same day as the ozone design value, and these readings are comparable, it is recommended that the median of the 6-9 a.m. NMHC/NO_x ratios observed on the five highest ozone days (with accompanying NMHC and NO_x data) be used as an estimate of the prevailing NMHC/NO_x ratio for the city. Following the recommendations from Section 3.2.2, when data from more than one monitoring site are available, the 6-9 a.m. ratios from each of these sites should be averaged on each day. The estimate of the ratio for use with EKMA is the median of these five average ratios.

Table 3.3 presents NMHC/NO_x ratios at seven RAPS sites (101 to 107) for three time periods: (1) the entire oxidant season (June-October), (2) the day with the second highest ozone concentration and (3) five high ozone days.* The comparison of interest is between the NMHC/NO_x ratio on the day with the second highest ozone concentration and the median ratio of the five high ozone days (hereafter referred to as the median ratio). Good agreement is found between

---

* The high ozone days were selected following application of quality control procedures described by Hunt et al.,[5,6] to the preliminary RAPS hourly data. Additional checks were also made for spatial continuity across the monitoring network.

TABLE 3.3 Comparison of $NMHC/NO_x$ Ratios for Selected Sites in St. Louis, 1976

(1) No.	(2) Location	(3) Seasonal $(\overline{NMHC})_{6-9}$ ppmC	(4) Seasonal $(\overline{NO_x})_{6-9}$ ppm	(5) Seasonal $(\overline{NMHC/NO_x})_{6-9}$	(6) Seasonal Median $(NMHC/NO_x)_{6-9}$	(7) $(NMHC/NO_x)_{6-9}$ for 2nd Max O_3	(8) Median $(NMHC/NO_x)_{6-9}$ on 5 days with high O_3 and NMHC, NO_x
1	Site 101	.67	.066	10.1	8.9	-	9.7
2	Site 102	.59	.094	6.2	5.5	9.1	7.1
3	Site 103	.38	.072	5.3	5.4	6.2	5.2
4	Site 104	.66	.074	9.0	8.6	6.4	6.4
5	Site 105	.75	.083	9.0	7.8	-	12.4
6	Site 106	.62	.078	7.9	8.1	6.5	6.8
7	Site 107	.65	.074	8.8	9.0	11.4	9.9

these two measures of the NMHC/NO_x ratio at the five sites where the comparison can be made. The largest difference is found at Site 102 with values of 9.1 for the day with the second maximum ozone concentration versus 7.1 for the median ratio of the five high days.

Similar comparisons are presented in Table 3.4 for the sites listed in Table 3.1. In order to conduct these comparisons, given the sparseness of precursor data at some of these sites, the NMHC/NO_x ratio on the highest ozone day with accompanying NMHC and NO_x data is used. Again, good agreement is found at the majority of these sites between the ratio observed on the high ozone day(s) and the median ratio, i.e., columns (3) and (4) of Table 3.4. A review of NMHC data for these high ozone days revealed that NMHC levels tended to be higher on these days. Table 3.5 confirms this characteristic of precursor concentrations at RAPS Sites 101 to 107. Thus, greater confidence can be placed in the ratio estimated on these high ozone days.

3.2.5 Default NMHC/NO_x Ratios

In order to apply EKMA to a specific city, both the ozone design value and the prevailing NMHC/NO_x ratio must be known. Frequently, however, ambient measurements of NMHC and NO_x may not be readily available for the city under review. To accomodate such a situation, default NMHC/NO_x ratios have been estimated for use with EKMA. These ratios are based on data from 14 sites in cities with varying emission patterns and meteorological conditions. Of 25 locations reviewed, these sites are considered most appropriate for estimating default ratios, because they meet the following criteria:

1) The sampling period is at least two weeks in duration, in order

TABLE 3.4 Comparison of NMHC/NO_x Ratios on High Ozone Days for Selected Cities*

(1) Site	(2) Median NMHC/NO_x Ratio (All Data)	(3) Median NMHC/NO_x Ratio on Five Highest O_3 Days With NMHC, NO_x Data	(4) (NMHC/NO_x) Ratio on day with Highest O_3 and NMHC, NO_x Data
Austin	10.1:1	10.0:1	9.1:1
Corpus Christi	18.5:1	21.3:1	21.3:1, 47.3:1 **
El Paso (1)	9.3:1	9.8:1	9.8:1
El Paso (A.P.)	10.0:1	14.0:1	14.0:1
Houston (Mae Dr.)	7.5:1	7.5:1	12.5:1
Los Angeles	9.8:1	10.2:1	8.3:1, 10.9:1 **
San Antonio	11.2:1	7.8:1	6.1:1
Aldine, TX	11.9:1	10.0:1	10.0:1
Azusa, CA	8.5:1	8.0:1	7.3:1, 7.9:1 **
Canton, OH	7.3:1	9.5:1	5.4:1
Dayton, OH	12.9:1	11.8:1	8.0:1
Groton, CT	9.5:1	8.8:1	7.2:1, 8.8:1 **
St. Louis***	7.6:1	8.5:1	7.5:1

* All NMHC, NO_x and ratio data refer to 6 a.m. - 9 a.m. LDT values.

** Two days with identical O_3 concentrations.

*** Composite of Sites 101 - 107.

TABLE 3.5 Comparison of Concentrations of NMHC and NO_x on High Ozone Days With Seasonal Mean Concentrations at RAPS Sites

(1) Site Location	(2) Seasonal $NMHC_{6-9}$	(3) Max O_3 Day $NMHC_{6-9}$	(4) 5 High O_3 Days* $NMHC_{6-9}$	(5) Seasonal NOX_{6-9}	(6) Max O_3 Day NOX_{6-9}	(7) 5 High O_3 Days* NOX_{6-9}
101	.67	ND	1.49	.066	.190	.134
102	.59	1.93	1.25	.094	.339	.176
103	.38	.97	.72	.072	.177	.105
104	.66	ND	1.04	.074	ND	.156
105	.75	1.94	1.95	.083	.179	.161
106	.62	1.45	1.55	.078	.171	.201
107	.65	2.26	1.21	.074	.301	.136

NOTE: Concentrations are ppmC for NMHC and ppm for NO_x.

ND - No data

* - Five highest ozone days at each site with accompanying NMHC and NO_x data.

to diminish the likelihood of a biased sample due to a single set of prevailing synoptic conditions.

2) At least 10 days of valid measurements for each parameter are available, so that extreme values can be eliminated when estimating 90th and 10th percentile NMHC/NO_x ratios.

3) The site is located in an urban or suburban area, and if in a suburban area, the site is not dominated by point sources of industrial organics.

4) The sampling has been conducted since 1974, in order to minimize the likelihood that ratios have been appreciably altered due to emission control programs.

Summary statistics for the 14 sites meeting the above criteria were presented previously in Table 3.1.

In the absence of ambient NMHC and NO_x data, the default ratio recommended for use with EKMA is a value of 9.5:1. This value is the median of the typical ratios observed in these cities on high ozone days, i.e., it is the median of the ratios listed in column (7) of Table 3.1, rounded to the nearest 0.5. Some measure of the range of possible values for the default ratio also seems desirable. To obtain a conservative measure, the 10th percentile and 90th percentile ratios observed at these sites are used. Estimates are based on the median of the ratios listed in columns (8) and (9) of Table 3.1. The medians of the 90th and 10th percentile ratios are, respectively, 15.9 and 5.9:1. Rounding these values gives default ratios of 16:1 and 6:1. Thus, in the absence of ambient measurements of the ratio, Figure 3.6 may be used to relate the sensitivity of maximum afternoon ozone levels to changes in upwind precursor levels.

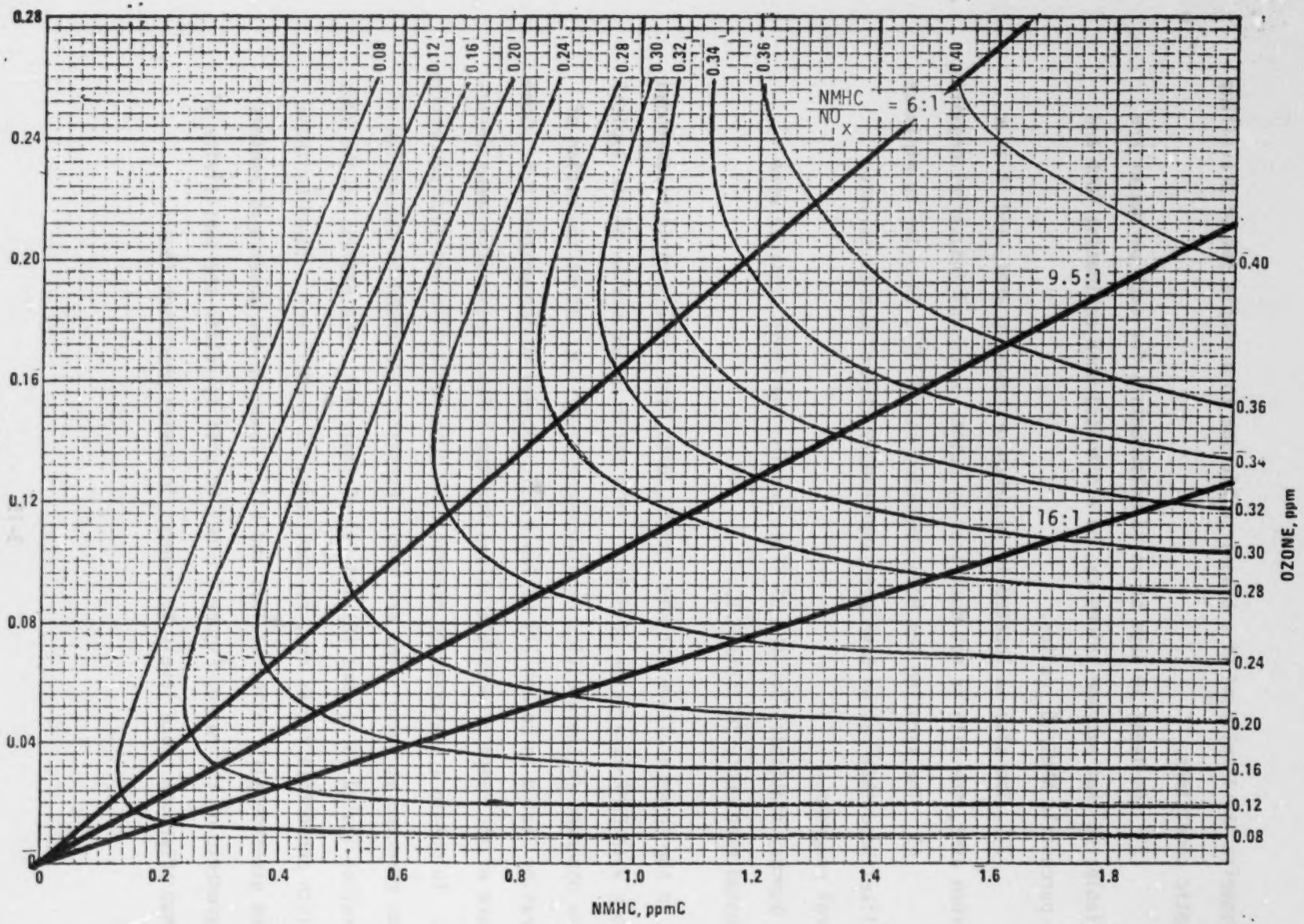

FIGURE 3.6 Sensitivity of maximum afternoon ozone concentrations to precursor concentrations, given default NMHC/NO_x ratios.

3.3 Summary and Recommendations

A review of ambient data on ozone, NMHC and NO_x concentrations from a number of cities has been conducted. Particular emphasis has been placed on data collected as part of the RAPS program in St. Louis during 1976. Significant findings from the study are:

1. NMHC and NO_x concentrations have very pronounced diurnal patterns at typical urban monitoring sites. Peak or near peak concentrations occur during the period 6-9 a.m. LDT.
2. The more distant the site is from a large urban area, the less pronounced is the diurnal variation and the lower are the concentrations.
3. Because of problems associated with measuring NMHC levels using an FID instrument, there is considerable uncertainty in individual NMHC readings. Studies have shown, however, that relative errors are less at higher concentration values.
4. There appears to be good agreement between the 6-9 a.m. $NMHC/NO_x$ ratio observed on the second highest ozone day and ratios observed on other high ozone days.
5. A typical ratio from a cross section of urbanized areas appears to be about 9.5:1.

These findings have several implications for how the ratio used in EKMA should be estimated. As was previously noted, the use of the 6-9 a.m. $NMHC/NO_x$ is considered to be consistent with the results from smog chamber experiments on which EKMA is based. Since both NMHC and NO_x levels are higher during this

period, greater confidence can be placed in the estimate of this ratio. However, because of the uncertainties in individual NMHC readings, use in EKMA of NMHC/NO_x ratios calculated at a single site for a single day is not recommended. Considering FID instrument reliability and model sensitivity, the suggested procedures for calculating NMHC/NO_x ratios for use in EKMA are:

1. If precursor measurements from more than one urban site are available for the same day as the ozone design value, and the individual ratios at each site do not differ by more than 50 percent from the average ratio, then the EKMA ratio (ER) is the average of the individual 6-9 a.m. NMHC/NO_x ratios. A review of instrument operating characteristics and data quality should be conducted prior to calculating the average ratio and performing the comparisons.

$$ER = \frac{\sum_{i=1}^{n} (R_i)}{n} = \bar{R}$$

where

R_i = 6-9 a.m. (NMHC/NO_x) ratio at Site i

$\bar{R}$ = the average ratio

n = the number of sites

Example

Given: The NMHC/NO_x ratios for St. Louis in Table 3.3, column (7).

Find: The NMHC/NO_x ratio for use in EKMA

Solution:

Ratio data are available for five of the seven central

sites. First calculate the average ratio,

$$\bar{R} = \frac{9.1 + 6.2 + 6.4 + 6.5 + 11.4}{5}$$

$$\bar{R} = 7.9$$

Note that all the ratios are within $\pm$ 50% of $\bar{R}$, i.e., all the ratios are between 4.0 and 11.9. Then, the EKMA ratio is given by,

$$ER = \bar{R} = 7.9$$

2. If only one site measuring both NMHC and NO_x is available, or if the values from different sites are not comparable (i.e., some ratios differ by more than 50% from the mean ratio), the following procedure is recommended. The ratio for use with EKMA is calculated as the median of the ratios observed on the five highest ozone days (with accompanying NMHC and NO_x data).

$$ER = \text{median} \left\{ R_j \right\} \text{, for a single site}$$

or

$$ER = \text{median} \left\{ \bar{R}_j \right\} \text{, for multiple sites}$$

where

j = a high day, and $j = 1,2,\ldots,5$

Example

Given: Assume that only RAPS Site 101 is available for St. Louis. The NMHC/NO_x ratios on the five days with high ozone and accompanying precursor data are 8.8, 8.6, 15.5, 9.7 and 14.3.

Find: The NMHC/NO_x ratio for use in EKMA.

Solution:

Since only one site is available, the EKMA ratio is given by,

$$ER = \text{median} \left\{ 8.8, 8.6, 15.5, 9.7, 14.3 \right\}$$

$$ER = 9.7$$

3. If ambient NMHC and NO_x data are not available, the use of the default ratio is recommended. The default ratio for use in EKMA is 9.5:1. As a measure of the uncertainty in estimating precursor controls introduced by the use of the default ratio, estimates using ratios of 16:1 and 6:1 can be made as well.

3.4 References

1. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors, EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

2. D. J. Londergan and L. G. Polgar, Measurement Program for Ambient O_3, NO_x and NMHC at Portland, Maine--Summer 1974, Unpublished Report, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1975.

3. Survey of Users of the EPA Reference Method for Measurement of Non-Methane Hydrocarbons in Ambient Air, EPA-650/4-75-008, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1974.

4. Hydrocarbon Measurement Discrepancies Among Various Analysers Using Flame-Ionization Detectors. EPA-600/4-75-010, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1975.

5. W. F. Hunt, et al., "The Application of Quality Control Procedures to the Ambient Air Pollution Problem in the U.S.A.," presented at the 20th Annual European Organization for Quality Control Conference in Copenhagen, Denmark, June 1976.

6. T. C. Curran, et al., "Quality Control for Hourly Air Pollution Data," presented at the 31st Annual Technical Conference of the American Society for Quality Control, Philadelphia, Pennsylvania, May 1977.

7. Interim Guidance on Air Quality Models, OAQPS 1.2-080, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1977.

8. Guidelines for the Interpretation of Air Quality Standards, OAQPS 1.2-008, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1974.

4.0 Variation Of Ozone and Precursor Levels In and Near Urban Areas

4.1 Introduction

4.1.1 Purpose

The purpose of Section 4 is to provide estimates of ambient ozone and precursor levels typically found upwind and downwind of urbanized areas. Particular emphasis is placed on concentrations observed upwind of urban areas on those days experiencing high oxidant levels.

4.1.2 Background

In Reference 1 and Section 5 of this report, it is concluded that unscavenged ozone remaining aloft at night is the facet of transport from upwind cities likely to exert the greatest impact on maximum ozone concentrations in urban areas, with a lesser impact also arising from transported organics. The principal difficulty in measuring transported ozone and in interpreting the results is having to rely primarily on surface measurements to estimate ozone levels aloft. In the absence of locally appropriate data on the breakup of nocturnal inversions, surface measurements of ozone between 1100 and 1300 LDT are suggested for use in estimating ozone which is advected aloft.[1] A discussion of the problems associated with using surface measurements to estimate ozone levels aloft is contained in Section 3.2 of Reference 1.

Ozone data from monitoring networks around cities reporting to SAROAD were examined in an effort to determine typical concentrations of transported ozone and precursors on days experiencing high concentrations of ozone. Meteorological data from the nearest National Weather Service (NWS) reporting station were used to identify the predominant wind flow on high ozone days, and thus, the appropriate upwind monitoring site. Problems were frequently encountered

when trying to make such estimates, resulting primarily from the absence of suitable upwind monitoring sites.

Ambient precursor data upwind and downwind of urban areas are sparse. A survey of data on ambient precursor levels in rural areas was presented in Section 2. Rural non-methane hydrocarbon levels as high as 200 ppbC were found. This section focuses on precursor concentrations in the vicinity of urban areas. The data base found most suitable for this analysis of precursor gradients is the St. Louis RAPS for 1976. The RAPS ground sampling network is shown in Figure 3.2. All sites provided continuous measurements of ambient ozone, non-methane hydrocarbon and oxides of nitrogen concentrations. Measures for other selected pollutants and meteorological variables were also provided.

4.2 Ozone Concentrations Measured Upwind of Urban Areas

For a large number of cities, suitable upwind sites were not available in SAROAD. Major problems included: (1) no monitoring site located upwind and/or outside the influence of an urban plume, (2) the wind field was poorly defined (i.e., an upwind site could not be determined) and (3) sites were subject to localized influences, e.g., nearby NO_x sources. These problems are understandable, because most networks are not designed to measure levels of ozone entering a city but rather maximum ozone concentrations which typically occur along the predominant downwind direction from the city.

Upwind ozone measurements on high ozone days for Philadelphia, Washington, Pittsburgh and Cleveland are presented in Table 4.1. As the values in the table indicate, average ozone concentrations measured upwind of these cities during the 1100-1300 LDT period on high ozone days are typically above the NAAQS of 0.08 ppm. Similar findings are reported by Cleveland, et al. in an

TABLE 4.1 Upwind Ozone Concentrations for Selected Cities on High Ozone Days During 1975

(ppm)

City	Downwind Site Max O_3 PPM	Wind* Direction DEG(10's)	Wind* AVG.SPD MPH	Upwind Site AVG. O_3 11-1300 LDT PPM
Philadelphia, PA	.33	23-23-22	7.5	.09
DWN = Bristol, PA	.29	22-23-23	6.6	ND
UP = Norristown, PA	.22	22-26-22	7.9	.09
	.18	30-24-22	7.9	.10
	.17	23-23-24	7.1	.10
Washington, D.C.				
DWN = Suitland, MD	.26	28-22-16	4.2	.13
UP = Fairfax, VA	.22	29-14-13	2.7	.13
	.18	35-28-22	4.5	.09
	.18	23-23-22	10.1	.12
Pittsburgh, PA				
DWN = Charleroi, PA	.23	06-06-34	3.0	ND
UP = Baden	.20	31-27-27	10.1	.09
	.19	08-32-06	3.2	.07
	.19	30-28-32	5.5	.05
	.15	10-02-06	4.6	.06
Cleveland, OH	.23	21-23-36	6.0	.09
DWN = Painesville, OH	.18	22-18-24	6.8	.09
UP = Medina, OH	.16	27-32-32	6.8	.12
	.16	27-29-30	8.9	.12

ND No Data

* Wind direction is expressed in tens of degrees, at three hourly periods: 1100, 1400 and 1700 LDT.

extensive study of ground level ozone data from the Northeast.[3]

When calculating upwind ozone concentrations, some discretion can be used in selecting an appropriate upwind monitoring site. Strictly speaking, the site does not have to be directly upwind of the city. As long as the site is not directly influenced by the urban plume from the city, it may be used as an upwind site. For example, in Figure 4.1, which depicts ozone monitoring sites in and around Philadelphia, the site located in Norristown can be taken as an upwind site on days with northeasterly flow.[4]

The spatial distribution of the RAPS monitoring sites enables upwind/downwind ozone concentrations to be determined under most wind flow patterns (see Figure 3.2). Table 4.2 lists upwind ozone concentrations averaged between 1100-1300 LDT for nine high ozone days in St. Louis during 1976. These upwind concentrations range from a low of 0.06 ppm to high of 0.12 ppm, with a median value of 0.07 ppm.

4.3 Urban Precursor Variations

The data used to define the relative magnitude of precursor concentrations across St. Louis are shown in Table 4.3. The table shows upwind, core and downwind concentrations of NMHC and NO_x for nine representative high ozone days in 1976.* These days were selected on the basis of the ozone concentration level as well as on a relatively consistent wind flow pattern across the RAPS monitoring network. In all cases studied, the peak precursor concentrations

---

* Core sites are those sites within 4 km of Site 101, i.e, Sites 101 through 107.

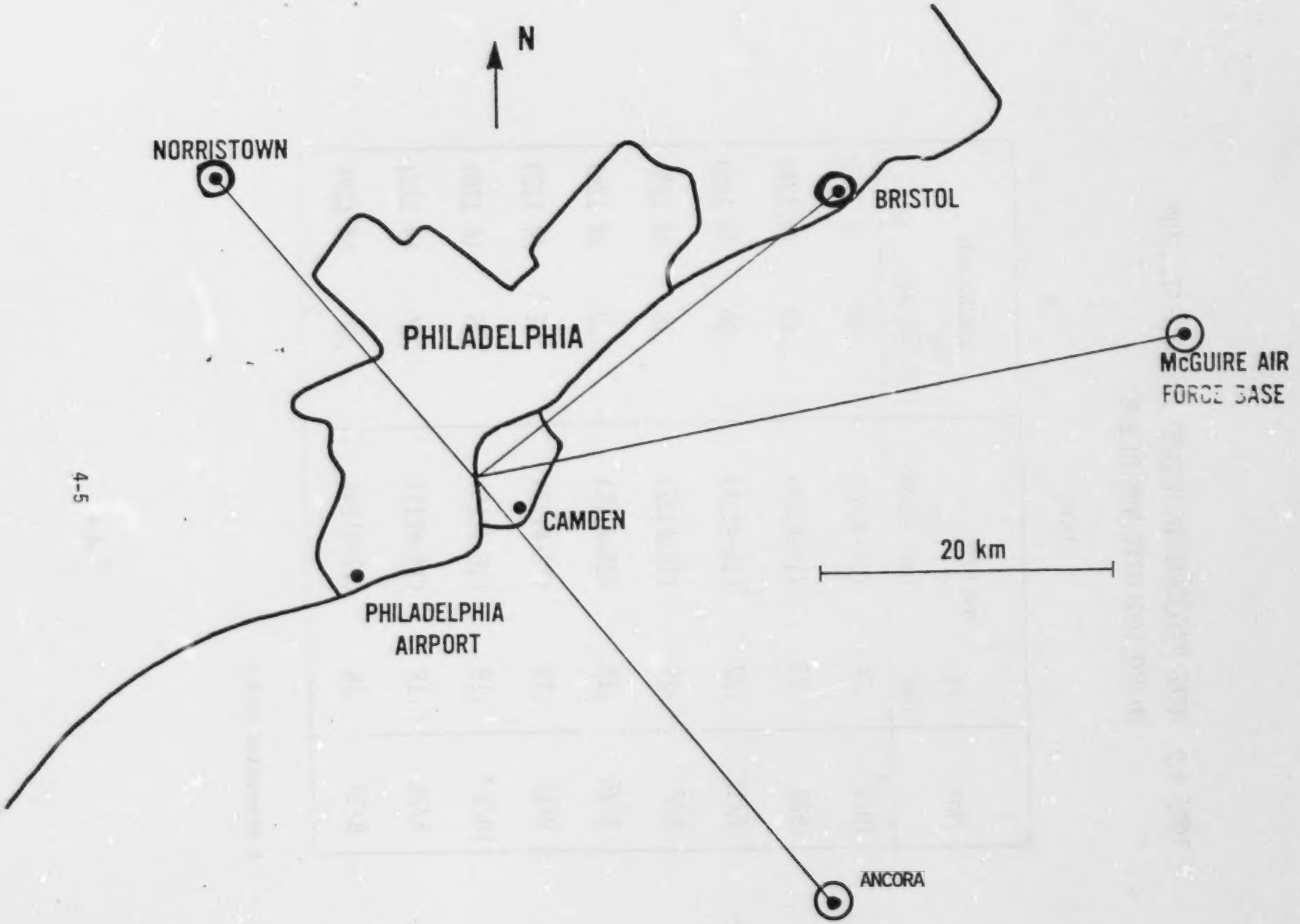

FIGURE 4.1 Ozone monitoring sites around the Philadelphia-Camden metropolitan area.

TABLE 4.2 OZONE CONCENTRATIONS MEASURED UPWIND OF ST. LOUIS ON NINE HIGH OZONE DAYS IN 1976

(ppm)

DATE	MAX SITE O_3 MAX	(HR. - SITE)	UPWIND SITE O_3 1100-1300 AVG	SITE
10/1 *	.24	(14-#102)	.07	(# 124)
6/8	.22	(16-#115)	.12	(# 124)
7/13	.22	(15-#114)	.09	(# 125)
6/7	.20	(15-#122)	.10	(# 125)
8/25	.19	(13-#115)	.10	(# 124)
9/17	.19	(12-#112)	.06	(# 122)
10/2 *	.19	(16-#115)	.06	(# 124)
8/26	.18	(13-#115)	.07	(# 125)
8/27	.18	(11-#114)	.07	(# 124)

* Stagnation period

TABLE 4.3
SIGNIFICANCE OF TRANSPORTED PRECURSOR CONCENTRATIONS
(NMHC in ppmC - NO_x in ppm)

St. Louis

Date (1976)	Pollutant	Representative 6-9 a.m. Mean Concentrations		
		Upwind* (Site #, km)	Core** (Site #)	Downwind* (Site #, km)
June 1	NMHC	0.05 (115, 27)	0.41 (106)	0.15 (118, 20)
	NO_x	< 0.01 (115, 27)	0.09 (104)	0.08 (118, 20)
June 7	NMHC	0.04 (118, 20)	2.98 (105)	0.10 (122, 40)
	NO_x	0.01 (124, 40)	0.23 (101)	0.01 (122, 40)
June 8	NMHC	ND	2.16 (105)	0.20 (115, 27)
	NO_x	< 0.01 (124, 40)	0.12 (102)	0.04 (115, 27)
July 19	NMHC	0.04 (121, 25)	0.57 (101)	0.02 (118, 20)
	NO_x	0.02 (122, 40)	0.05 (101)	< 0.01 (124, 40)
July 30	NMHC	ND	1.75 (101)	0.56 (121, 25)
	NO_x	ND	0.13 (107)	0.08 (121, 25)
August 4	NMHC	ND	1.28 (104)	0.88 (122, 40)
	NO_x	0.01 (124, 40)	0.11 (101)	0.02 (122, 40)
August 12	NMHC	< 0.01 (118, 20)	0.80 (107)	0.34 (122, 40)
	NO_x	< 0.01 (124, 40)	0.09 (102)	0.03 (122, 40)
August 17	NMHC	0.07 (116, 21)	1.09 (107)	0.49 (120, 20)
	NO_x	0.02 (123, 40)	0.15 (103)	0.05 (120, 20)
August 18	NMHC	0.16 (123, 40)	1.68 (107)	0.29 (125, 40)
	NO_x	0.03 (123, 40)	0.09 (107)	0.06 (125, 40)

* Furthest Upwind, Downwind Sites With Available Data For Each Pollutant

** Maximum 6-9 a.m. Average Value For Each Pollutant Within 4 km Of Site 101

were observed over center city. The center city concentration levels were typically about three to thirty times greater than upwind-downwind values. Figures 4.2 and 4.3 present average 6-9 a.m. NMHC and NO_x concentrations with distance from center city, along a north-south axis, during the oxidant season (June-October). The use of seasonal average concentrations should provide a robust estimate of the precursor gradients across the St. Louis urban area.

Based on a review of the RAPS data, reasonable estimates for precursor transport into an urban area appear to be a concentration range for NMHC of 0.05-0.30 ppmC and for NO_x of < 0.01-0.05 ppm. The lower limit of the concentration range for each precursor is assumed to represent precursor levels typical of long range transport into an isolated city. The upper limit of the concentration range for each precursor is assumed to represent precursor levels typical of transport into a city that is about 40 kilometers downwind of a medium/large city.

4.4 Summary

Ozone gradient data (upwind versus downwind) are difficult to obtain because of limited data from appropriate upwind sites. Such data as have been examined indicate a sizable increase in ozone concentrations downwind from major cities during days with meteorological conditions conducive to ozone formation. Surface measurements upwind from major cities not clearly dominated by the urban plume from another city farther upwind suggest long range transport values for ozone ranging from 0.05-0.13 ppm. Such values are reasonably consistent with concentrations observed aloft overnight in balloon experiments.[5]

The sparse data available on precursor levels entering urban areas from

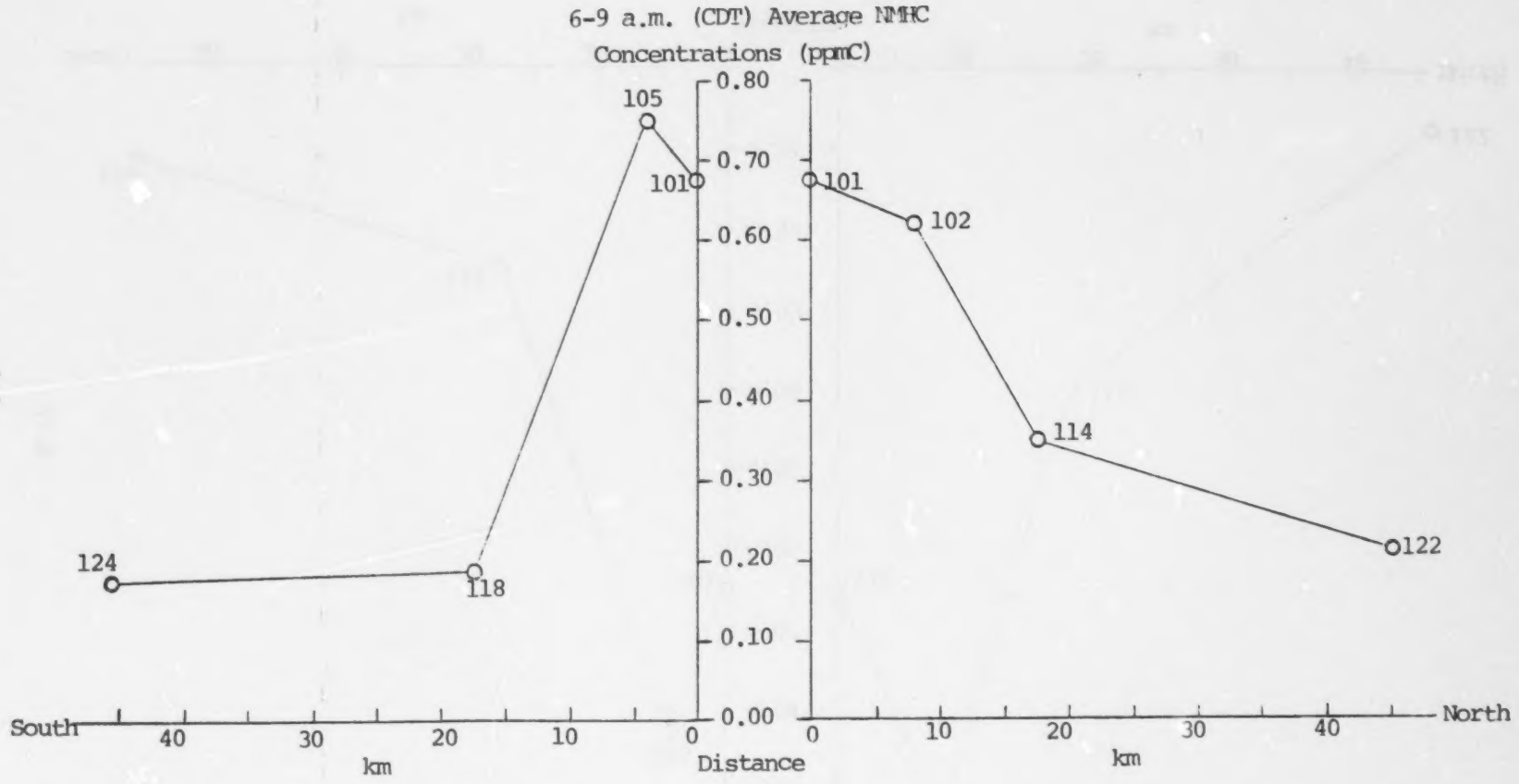

FIGURE 4.2 Variation of 6-9 a.m. Average NMHC With Distance From Site 101 (June - October 1976)

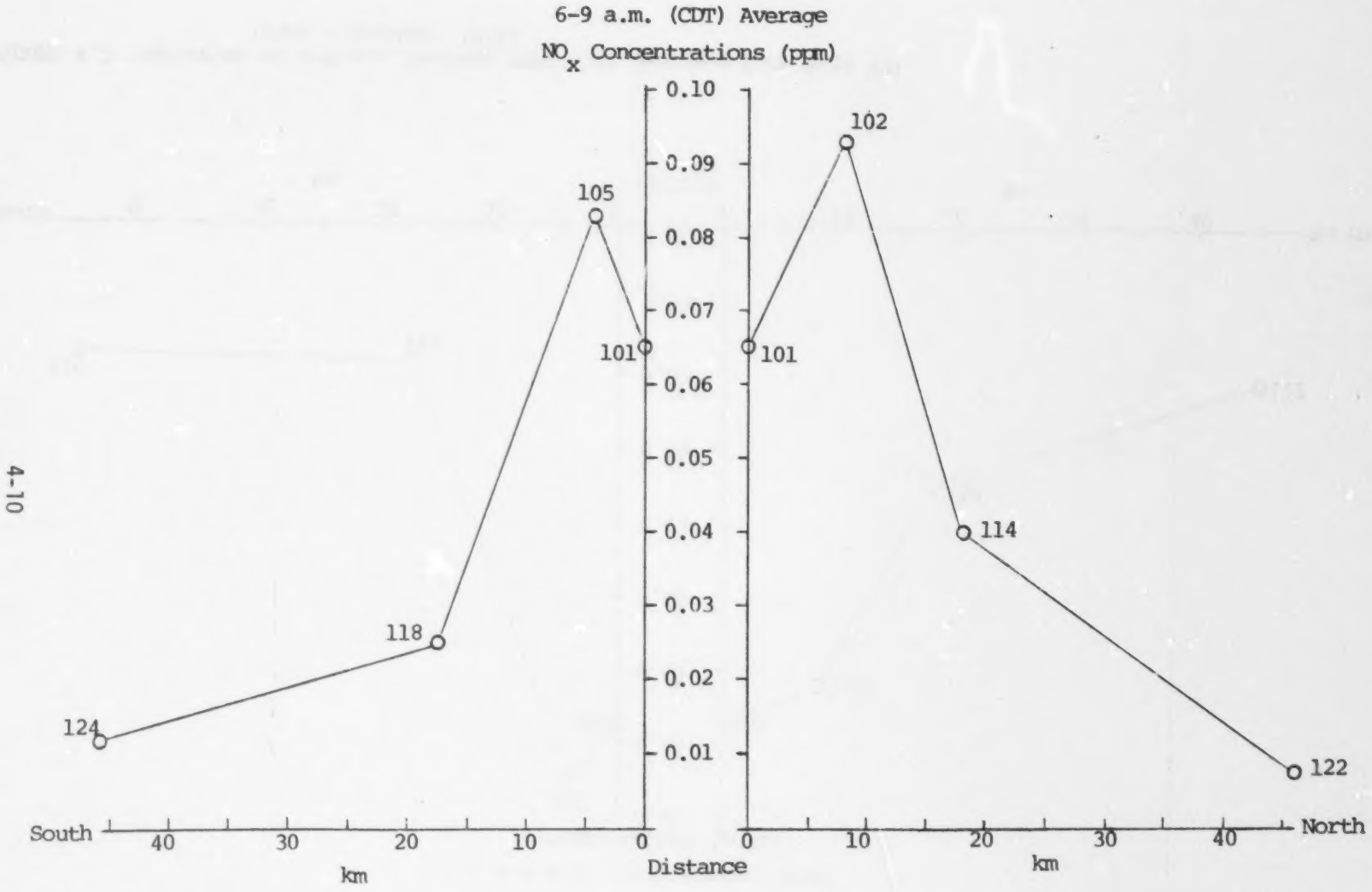

FIGURE 4.3 Variation of 6-9 a.m. Average NO_x With Distance From Site 101 (June - October 1976)

rural regions indicate that these levels are normally low. Information in Section 2 and this Section suggest that non-methane hydrocarbon levels from about 0.05 to 0.30 ppmC, and nitrogen oxide levels from < 0.01 to 0.05 ppm are typical ranges for precursor transport into an urban area. The upper limit of these ranges may be suggestive of some impact of upwind urban areas or re-circulation from the same urban area. On high oxidant days, the morning (6-9 a.m.) NMHC and NO_x values in urban centers are about ten or more times greater than in adjacent rural areas. Simulations with the kinetics model in EKMA (Section 5) suggest that these estimates of precursor background levels will generally not contribute significantly to the synthesis of high ozone levels in the vicinity of an urban area.

4.5 References

1. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors, EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

2. Investigation of Rural Levels as Related to Urban Hydrocarbon Control Strategies. EPA-450/3-75-036, U.S. EPA, Research Triangle Park, North Carolina, March 1975.

3. W. S. Cleveland, et al., The Analysis of Ground Level Ozone Data From New Jersey, New York, Connecticut, and Massachusetts: Transport From the New York City Metropolitan Area, Bell Laboratories, Murray Hill, New Jersey, 1976.

4. W. S. Cleveland and B. Kleiner, "The Transport of Photochemical Air Pollution From the Camden-Philadelphia Urban Complex," Environmental Science & Technology, Vol. 9, No. 9, September 1975.

5. E. Robinson, F. Vukovich and D. H. Pack, "International Conference on Oxidants 1976 -- Analysis of Evidence and Viewpoint. Part V. The Issue of Oxidant Transport." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

5.0 The Impact of Inter-Urban Pollutant Transport on Oxidant Concentrations

5.1 Introduction

The production of ozone from precursor emissions in an urban area can be significantly affected by pollutants generated in areas upwind and transported into the urban area. To assess the impact of these transported pollutants, several simulations were conducted using the kinetics model underlying the Empirical Kinetic Modeling Approach. This Section discusses these simulations and their significance in terms of ozone-precursor relationships.

The simulations conducted in this study attempted to provide answers to two major questions. The first question is "What aspect of the transport of pollutants has the most significant effect on the peak ozone concentration found in the vicinity of an urban area?" Several pollutants that affect oxidant production, including ozone, non-methane hydrocarbons, oxides of nitrogen and aldehydes, may be transported into an urban area. A number of kinetics model simulations were performed to determine which transported pollutants have the greatest impact on peak ozone concentrations. These simulations also included evaluation of the relative importance of ozone and precursor transport in a layer near the ground versus in a layer aloft.

The second major question is "What is the impact of transported ozone under varying conditions?" A number of model simulations were conducted to determine how the impact of transported ozone is affected by variations in dilution rate, temporal emission distribution and sunlight intensity. Also investigated was how the impact of transported ozone varies with the transported ozone concentration itself, the level of local emissions and the prevailing NMHC/NO_x ratio. Although most of these simulations were intended to

assess the impact of pollutant transport for a current range of situations, some additional simulations were also conducted for situations anticipated when the National Ambient Air Quality Standard for oxidants is approached.

5.2 The Simulation Model

All simulations discussed here employed the kinetics model used in generating the standard and city-specific isopleths presented in Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors.[1] This kinetics model is discussed further by Dodge[2] and by Whitten and Hogo.[3]

An important assumption inherent in this kinetics model is that pollutant concentrations are uniformly mixed throughout a column of air extending through the entire mixed layer. As mixing increases to greater heights, the model assumes that entrained air is instantaneously mixed throughout the enlarged mixed layer. Similarly, the model also assumes instantaneous upward mixing of emissions. These assumptions could significantly affect the timing, and possibly the quantitative impact, of the interaction of transported pollutants and local emissions. Thus, this study is intended only to compare relative impacts of various pollutant transport conditions rather than to assess the absolute impact of any single set of pollutant transport conditions.

5.3 Conditions Simulated

Table 5.1 shows the basic set of conditions simulated in this study. Reference 1 provides a more extensive discussion of the nature of these variables. As shown in Table 5.1, these conditions differ from those used in deriving the standard set of isopleths presented in Reference 1. While the standard isopleths are based on probable worst-case meteorological conditions,

TABLE 5.1

Base Set of Conditions Assumed in Kinetics Model Simulations

Data Required	Conditions Assumed in Standard Isopleths	Conditions Assumed in this study
Parameters Affecting light Intensity	34°N, 118°W June 21	40°N, 75°W, Sept. 15
Dilution rate	3%/hour	13%/hour and 29%/hour
Relative Emission rates	All emissions occur by 8 a.m. LDT	Time: by 8 a.m. — Relative Emission Rates*: 100% 8 - 9 a.m. — 28.5% 9 -10 a.m. — 23.3% 10 -11 a.m. — 15.0% 11 a.m. -12 noon — 6.3% after 12 noon — no emissions
Initial Relationship of NO_2 and NO_x	$NC_2 = 25\% \times NO_x$ $NO = 75\% \times NO_x$	$NO_2 = (15\% \times NO_x) + (O_3)_t$ ** $NO = NO_x - NO_2$

*Emission rates are normalized relative to emissions prior to 8 a.m. LDT.

**$(O_3)_t$ represents the ozone concentration transported into the city in the surface layer--see text.

the simulations in this study are intended to represent a typical range of conditions found throughout much of the United States during days experiencing high ozone concentrations.

The first item in Table 5.1 concerns parameters that affect the diurnal distribution of light intensity. They are used to determine photolytic rate constants in the kinetics model. At the time this study was conducted, it was only possible to use photolytic rate constant data for 40°N, 75°W on September 15 and for 34°N, 118°W on June 21. Since the highest ozone concentrations often occur in the late summer or early fall, the first of these two sets of data was used in these simulations. Nevertheless, these two sets of diurnal light intensity distributions are not radically different. Specifically, the June insolation has approximately a 17 percent higher peak insolation and a 10 percent higher integrated average light intensity between 8 a.m. and 5 p.m. local daylight time.

The second item in Table 5.1, dilution rate, is used to simulate the entrainment of relatively clean air from aloft as the mixing height increases, a process which results in dilution of concentrations within the mixed layer. In these simulations, the air above the mixed layer often contains significant concentrations of pollutants. However, the kinetics model first calculates dilution rate as if the entrained air were clean and then accounts separately for entrainment of pollutants.

Dilution rate, expressed here as percent per hour, is defined as the percentage increase in the mixing height that occurs over a period of an hour. Table 5.1 shows the two dilution rates used in this study. The mixing height was assumed to rise for six hours and to remain constant thereafter. Hence,

the total increases in mixing height for the 13%/hr and the 29%/hr dilution rates were approximately a twofold increase and approximately a fivefold increase, respectively.

The third item shown on Table 5.1 is relative emission rates. These are used to simulate the rates of emissions into the air parcel for each hour of the simulation. These rates are typically based on a hypothetical air parcel trajectory and an assumed spatial and temporal distribution of emissions encountered along this trajectory. The rates are then normalized relative to the emissions present at the beginning of the simulation (8 a.m. LDT). The mixing height was assumed in this study to begin increasing at 9 a.m., and so the calculation of rates of concentration addition required no adjustment of relative emission rates prior to this time.

In calculating the basic set of relative emission rates used in this study, the air parcel was assumed to remain at the center of the city until 9 a.m. At that time, the air parcel was assumed to begin moving downwind, reaching the edge of the city three hours later. The spatial distribution of emissions was assumed to be Gaussian in the direction of the wind, with the edge of the city having e^{-2} (about 0.14) of the emission density at the center of the city. The temporal distribution of emissions was obtained from a U.S. Department of Transportation study of traffic distribution in several cities.[4] The resulting set of relative emission rates as used in this study is shown in Table 5.1.

The derivation of relative emission rates in this study involved some simplifying assumptions, particularly those concerning the emission densities of areas traversed by the air parcel. Unfortunately, it is often quite difficult

to obtain more accurate information on air parcel trajectories and on spatial distributions of emissions. When such information is available, it is often suitable to use a more sophisticated model. Thus, these assumptions should reflect the accuracy appropriate for use in a kinetics model. In any case, this study also supplies information regarding the effect of several alternative assumptions in calculating relative emission rates.

The fourth variable shown in Table 5.1 is initial NO and NO_2 concentrations as a function of the initial NO_x concentration. Most NO_x emissions are largely NO. However, the fraction of NO_2 is increased by photochemically induced organic reactions and by reaction with ozone. As indicated in Table 5.1, the standard isopleths used a fixed initial NO_2/NO_x ratio, based on relatively low transported pollutant concentrations. On the other hand, the initial mixes of NO and NO_2 in these simulations were based on a ratio of NO_2/NO_x attributable to organic reactions and an adjustment according to the transported ozone concentration. In some simulations with high transported ozone concentrations, the initial NO was entirely NO_2, and the simulations began with an "excess" ozone concentration.

5.4 The Impact of Transport of Various Pollutants on Ozone Concentrations

Photochemical production of ozone in an urban area can be affected by transport of various pollutants from upwind areas. In particular, it is important to consider the transport of ozone, precursors (i.e., hydrocarbons and NO_x) and aldehydes.

A substantial number of studies have indicated that ozone can be transported over long distances between cities.[5] It is necessary to consider this ozone in terms of two atmospheric layers: (1) the surface layer (i.e., the

morning mixed layer), and (2) the layer aloft, particularly the layer that is above the mixed layer in the morning but within the mixed layer in the afternoon. Ozone transported in both atmospheric layers can react with NO according to the reaction $NO + O_3 \rightarrow NO_2 + O_2$. However, ozone transported in these two layers is added to the air parcel by different means, and it affects the concentrations at different times. The ozone transported in the surface layer is present in the air parcel prior to the simulation period and is simulated by adjusting the initial concentrations. The kinetics model assumes that both the transported ozone concentration and other pollutant concentrations are horizontally homogeneous in the vicinity of the primary air parcel. Thus, horizontal interchange with other air parcels is assumed not to affect the concentration in the primary air parcel. Ozone transported aloft, on the other hand, affects concentrations in the primary air parcel as the mixing height increases and the air parcel entrains this ozone from aloft. Thus, ozone transported aloft affects the air parcel concentrations in the late morning and in the afternoon. Unlike the ozone transported in the surface layer, the rate of addition of ozone aloft changes if the rate of the increase in the mixing height changes. A typical scenario is pictured conceptually in Figure 5-1.

Like the transport of ozone, the transport of precursors may also be considered in terms of two layers, i.e., transport in the surface layer and transport aloft. The pollutant concentration aloft is likely to be different from that in the surface layer, due both to differences in the meteorological history of the two layers of air and to incomplete vertical mixing of ground level emissions.

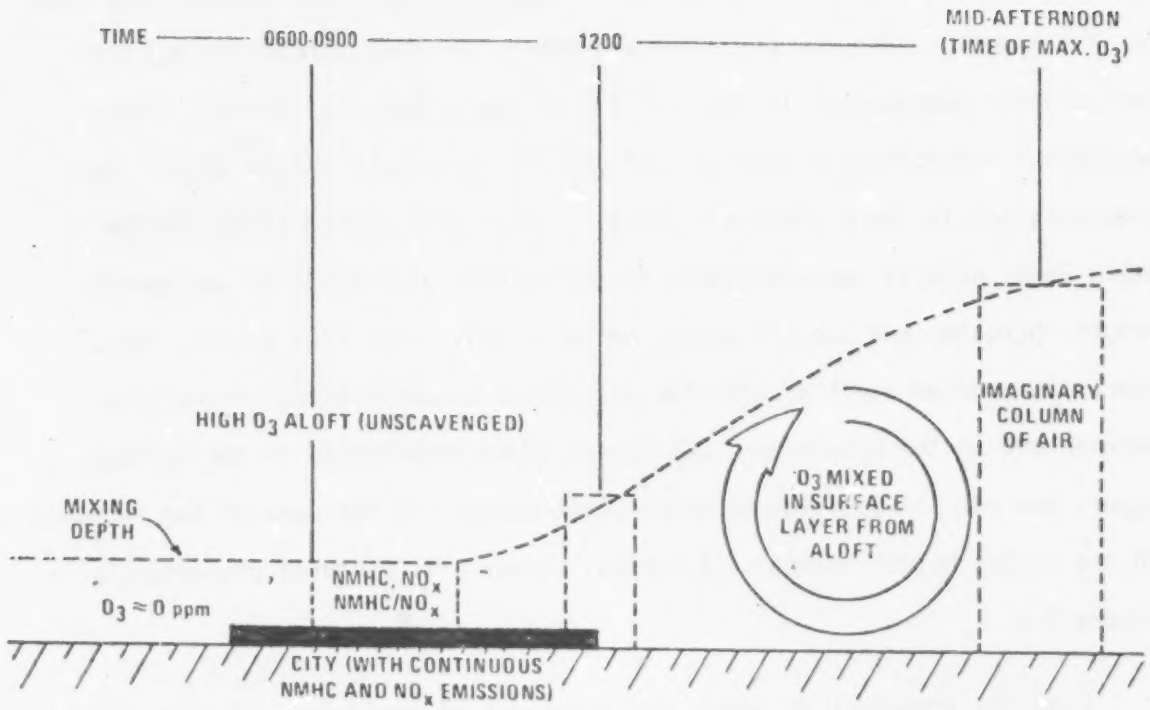

FIGURE 5.1 Role of ozone aloft on maximum surface ozone levels: a conceptual view

Unfortunately, it is difficult to make reasonable assumptions about the typical relationship between precursor concentrations at the surface and aloft. This study tested two alternative assumptions: (1) precursor concentrations aloft are equal to the concentrations in the surface layer, and (2) insignificant concentrations exist aloft. The true situation can probably be expected to fall between these two assumptions, but it is difficult to assess which assumption is more appropriate.

Another class of pollutants which may be transported in significant quantities is aldehydes. Aldehydes are both products and reactants in the photochemical production of ozone. As a result, in an air mass in which the photochemical pollutants have had ample time to react (an "aged air mass"), aldehyde concentrations may be a somewhat higher proportion of organic species than their proportion in emissions.

To compare the impact of the transport of these various pollutants, two approaches were used. The first approach simulated approximately the maximum pollutant concentrations that might be transported into an urban area. One would seldom expect all of these concentrations to be transported in the same air mass at the same time. However, this approach was not intended for estimating the maximum total impact of pollutant transport. Rather, it was intended to estimate and to compare the maximum impacts of the transport of <u>each pollutant</u> <u>separately</u>, considering the worst case for each pollutant. The second approach was based on the selection of more typical transported pollutant concentrations. This approach was intended to suggest the typical relative importance of the transport of various pollutants.

The first part of Table 5.2 shows the transported pollutant concentrations used in the comparison of worst cases. As indicated in the table, it was assumed that the approximate upper limit to the ozone concentration transported in the surface layer is less than the approximate upper limit to ozone concentrations transported aloft. This was based on the presumption that ground level scavenging could significantly affect early morning ozone concentrations in the shallow surface layer but does not affect ozone concentrations aloft. It was assumed that ozone concentrations transported aloft seldom exceed 200 ppb and that ozone concentrations transported in the surface layer will seldom exceed 120 ppb.

The transported precursor concentrations used in the comparison of worst cases represent the concentrations found within 40 kilometers downwind of St. Louis. These data are discussed in Section 4. Very few cities are within 40 kilometers of a city the size of St. Louis, and so very few cities should experience transported precursor concentrations as high as those indicated on Table 5.2.

As discussed previously, it is difficult to hypothesize the typical relationship between precursor concentrations transported aloft and the concentrations transported in the surface layer. However, it may be possible to make some generalizations about the relationship between the worst case precursor concentration transported aloft and the worst case precursor concentration transported in the surface layer. The worst case precursor concentrations transported into the city in the two layers probably occur under two different types of situations. The existence of high precursor concentrations transported in the layer aloft is probably dependent upon the occurrence of

TABLE 5.2

Conditions Assumed in Simulating the Transport of Various Pollutants

Comparison of Worst Cases

Pollutant	Transported Concentration
Ozone	Aloft: 200 ppb Surface Layer: 120 ppb
Precursors*	NMHC = .26 ppmC (90% butane, 10% propylene) NO_x = .04 ppm (100% NO_2)
Aldehydes	Significance tested by doubling initial concentrations

Comparison of Typical Cases

Pollutant	Transported Concentration
Ozone	120 ppb (in both layers)
Precursors*	NMHC = .10 ppmC (100% butane) NO_x = 0.0 ppm
Aldehydes	Negligible

*Two alternative assumptions are used in simulating precursor transport:

1. Concentrations transported aloft equal concentrations transported in the surface layer.
2. Concentrations transported aloft are negligible.

substantial emissions on a previous day, when mixing extended above the current surface layer. In contrast, the highest precursor concentrations transported in the surface layer probably occur when substantial emissions enter the layer during the evening or at night, when the mixed layer is shallow. Therefore, the highest precursor concentrations transported in the surface layer are likely to be substantially greater than the highest concentrations transported aloft, due to the substantially lower mixing height as well as the shorter time during which dilution can occur. As a result, the actual worst case impact of precursor transport is likely to be better represented by the assumption of negligible concentrations aloft than by the assumption that the concentration aloft equals the concentration in the surface layer.

Transported precursors differ significantly from urban emission in terms of the composition of the pollutant mix. The kinetics model simulations of smog chamber results suggest that the best representation of automotive exhaust with a butane-propylene mix uses 75% butane by ppmC.[2] However, a transported hydrocarbon mix is lower in reactivity, due to prior reaction of the more reactive species. Therefore, in these simulations, the 0.26 ppmC of transported hydrocarbons was arbitrarily chosen to be 90% butane and 10% propylene. The entire 0.04 ppm of NO_x was assumed to be NO_2.

Quantification of transported aldehyde concentrations is difficult, especially due to an absence of reliable measurements. Therefore, the worst case transport of aldehydes was simulated simply by doubling the 8 a.m. aldehyde concentrations. This may be considered as much an expression of the uncertainty in aldehyde measurements as of the potential impact of aldehyde transport. It seems unlikely that aldehyde transport would have such a large effect on urban aldehyde concentrations. Nevertheless, given the dearth of

reliable evidence on aldehyde concentrations, this should represent a reasonable upper boundary of aldehyde transport for this study.

The typical case of transported pollutant concentrations is presented in the second half of Table 5.2. These concentrations were chosen to reflect a scenario in which an upwind city is located a considerable distance from the city being modeled. As discussed by a number of authors, high ozone concentrations can be transported over long distances, but precursor concentrations tend to decrease rapidly with distance.[5] For this scenario, the transported ozone concentration was taken as 120 ppb. For simplicity, the ozone concentration transported in the surface layer was taken as equal to the concentration transported aloft. The precursor concentrations were closer to the background concentrations discussed in Section 2.

Simulations of precursor transport were conducted both for the assumption that concentrations transported aloft equal those transported in the surface layer and for the assumption that precursor concentrations transported aloft are negligible. Little evidence is available to indicate which assumption more closely approximates the typical case. In this case, the precursors will often be emitted into the transported air mass on some previous day, providing an opportunity for substantial mixing into the "layer aloft". Nevertheless, uncertainties about the mixing process and about the subsequent dispersion and transport in the layer aloft and in the surface layer make it difficult to estimate the relationship between precursor concentrations in the two layers. As indicated in Table 5.2, the 0.10 ppmC of transported hydrocarbons was assumed to consist entirely of butane, reflecting substantial reduction of the reactivity of the hydrocarbon mix due to reaction of the more reactive species.

Transported concentrations of both NO_x and aldehydes were assumed to be negligible.

Tables 5.3A and 5.3B show the impacts on peak ozone concentrations of worst case and typical case pollutant transport, respectively. The results shown on these tables suggest that the transport of ozone is more significant than the transport of other pollutants. The transport of concentrations of precursors for worst case conditions can also have a significant effect, particularly if concentrations transported aloft are as high as those transported in the surface layer. However, as discussed previously, the highest precursor concentrations transported aloft are likely to be substantially less than the highest concentrations transported in the surface layer. Table 5.3A suggests that if negligible concentrations aloft are assumed, the worst case impact of precursor transport is considerably less than the worst case impact of ozone transport. Table 5.3B suggests that the typical impact of precursor transport is much less than the typical impact of ozone transport. These two tables suggest that the impact of worst case precursor transport is comparable to the impact of a moderate level of ozone transport. Precursor transport thus appears to be occasionally significant but generally much less significant than ozone transport.

The results in Table 5.3A also suggest that increases in the initial aldehyde concentration have a negligible impact on peak ozone concentrations. In fact, an increase in aldehydes in one case caused a decrease in the peak ozone concentration. This may be due to an increase in the depletion of NO_x by the forming of such compounds as HNO_3.

Additional simulations were conducted to assess the relative significance

TABLE 5.3A

The Impact of Worst Case Transport of Various Pollutants on Peak Ozone Concentrations

NMHC/NO_x Ratio	Initial Concentrations HC	Initial Concentrations NO_x	Base Case Peak Ozone (no transport)	Increase in Peak Ozone Attributable to Pollutant Transport: Ozone Transport in Surface Layer and Aloft	Precursor Transport in Surface Layer	Precursor Transport in Surface Layer and Aloft	Aldehydes Transport
6	1.2 ppmC	0.2 ppm	328 ppb	67 ppb	24 ppb	48 ppb	10 ppb
10	1.4	0.14	332	53	26	40	3
16	1.76	0.11	321	44	34	48	-1
6	0.6	0.10	208	76	30	58	1
10	0.7	0.07	208	69	32	56	3
16	0.96	0.06	219	58	40	58	1
6	0.24	0.04	108	94	39	73	1
10	0.25	0.025	100	89	41	80	1
16	0.32	0.02	102	86	48	84	1
			Average:	71 ppb	35 ppb	61 ppb	2 ppb

TABLE 5.3B

The Impact of Typical Case Transport of Various Pollutants on Peak Ozone Concentrations

$NMHC/NO_x$ Ratio	Initial Concentrations HC	Initial Concentrations NO_x	Base Case Peak Ozone (no transport)	Increase in Peak Ozone Attributable to Pollutant Transport: Ozone Transport in Surface Layer and Aloft	Precursor Transport in Surface Layer	Precursor Transport in Surface Layer and Aloft
6	1.2 ppmC	0.2 ppm	328 ppb	43 ppb	6 ppb	9 ppb
10	1.4	0.14	332	33	3	3
16	1.76	0.11	321	25	2	2
6	0.6	0.1	208	49	7	11
10	0.7	0.07	208	44	4	5
16	0.96	0.06	219	37	1	2
6	0.24	0.04	108	64	9	14
10	0.25	0.025	100	60	4	6
16	0.32	0.02	102	58	2	4
			Average:	46 ppb	4 ppb	6 ppb

of ozone transported aloft and ozone transported in the surface layer. Specifically, simulations were conducted to compare the impact of 120 ppb of ozone transported aloft and the same concentration transported in the surface layer. Table 5.4 shows that the impact of ozone transported aloft is much greater than the impact of ozone transported in the surface layer. If consideration is given to ground level ozone scavenging, the comparison suggests even more strongly that ozone transported aloft is more significant than ozone transported in the surface layer.

5.5 The Impact of Ozone Transport Under Various Conditions

The results discussed in the previous section suggest that the best variable for characterizing a given transport situation is the ozone concentration transported aloft. This section presents the results of numerous simulations for various ozone concentrations transported aloft in a variety of situations.

The impact of ozone transported aloft is influenced by several factors that can be used to characterize a given day in a given city. These factors include the NMHC/NO_x ratio, the peak ozone concentration in the urban area, dilution rate, the relative emission rates,* and the diurnal pattern of light intensity. Table 5.1 and the discussion in Section 5.3 present the conditions used in simulating pollutant transport. Using this basic set of conditions, simulations were performed for various combinations of four concentrations of ozone aloft, the two dilution rates, and the nine pairs of initial NMHC and

---

* Emission rates are normalized relative to emissions prior to 8 a.m. LDT.

TABLE 5.4

The Impact of Ozone Transport in Different Atmospheric Layers

$NMHC/NO_x$ Ratio	Base Case Peak Ozone (no transport)	Increase in Peak Ozone Attributable to Ozone Transport	
		120 ppb Ozone Aloft	120 ppb Ozone in Surface Layer
6	328 ppb	37 ppb	11 ppb
10	332	29	5
16	321	26	0
6	208	36	12
10	208	33	12
16	219	30	8
6	108	40	24
10	100	38	25
16	102	37	24
		Average: 34 ppb	13 ppb

NO_x concentrations. These are shown in Figure 5.2. Additional simulations were performed for the four concentrations of ozone aloft and four selected NMHC/NO_x pairs with: (1) two alternative sets of relative emission rates, and (2) an alternative diurnal light distribution, as shown in Figure 5.3. As indicated therein, all these additional simulations were based on a dilution rate of 13%/hr.

Although this discussion focuses on the ozone concentration transported aloft, other transported pollutant concentrations were also varied in these simulations. The ozone concentration transported into the city in the surface layer in the early morning was in most cases assumed equal to the ozone concentrations transported aloft. The only exception to this was for the case of 200 ppb of ozone aloft, in which case the ozone concentration transported at ground level was assumed to be 120 ppb. The initial aldehyde concentrations were left at their "normal" mix ($[\text{formaldehyde}]_o = .02\ [\text{NMHC}]_o$ and $[\text{acetaldehyde}]_o = .03\ [\text{NMHC}]_o$) when the ozone concentration aloft was low (O_3 = 0 ppb or 40 ppb) and twice as high when the ozone concentration was high (O_3 = 120 ppb or 200 ppb). As discussed in the previous section, this adjustment is greater than might normally be expected, but this should not noticeably affect the estimated impact of pollutant transport.

These simulations did not incorporate the transport of NMHC or NO_x. The transport of these precursors can be assumed to cause an increase in the peak ozone concentration. However, the relative variations of the impact of pollutant transport under various conditions are assumed not to be affected by the presence or absence of transported precursors.

Table 5.5 presents the results of the simulations shown in Figure 5.2 for

FIGURE 5.2 Primary Set of Simulated Conditions*

Variable:	Ozone Concentration Transported Aloft	Dilution Rate	Initial Concentrations** NMHC: NO_x		
			6:1	10:1	16:1
Conditions Simulated	0 ppb	13%/hr	1.2/0.2	1.4/0.14	1.76/0.11
	40 ppb	29%/hr	0.6/0.1	0.7/0.07	0.96/0.06
	120 ppb		0.24/0.04	0.25/0.025	0.32/0.02
	200 ppb				

*Simulations were conducted for all combinations of ozone concentrations aloft, dilution rate, and initial concentrations. All simulations were based on the diurnal light distribution and the relative emission rates presented in Table 5.1.

**Each pair represents a simulation using the respective initial NMHC (in ppmC)/NO_x (in ppm).

FIGURE 5.3 Additional Conditions Simulated*

Simulations with Various Relative Emissions Rates Times (in LDT)

	Relative Emission Rates**		
	Base Case	Stagnation	Persistent Winds
Up to 8 A.M.	100%	100%	100%
8 - 9 A.M.	28.5	28.6	29.6
9 - 10 A.M.	23.3	24.5	13.1
10 - 11 A.M.	15.0	24.5	4.3
11 - 12 A.M.	6.3	25.0	-
12 - 1 P.M.	-	25.0	-
1 - 2 P.M.	-	26.6	-
2 - 3 P.M.	-	31.8	-
3 - 4 P.M.	-	39.6	-
4 - 5 P.M.	-	54.7	-

Ozone Concentration Transported Aloft

0 ppb
40 ppb
120 ppb
200 ppb

Initial Concentrations***

1.2/0.2	1.76/0.11
0.24/0.04	0.32/0.02

Simulations with different light intensity conditions

Light Intensity Conditions
40°N, 75° W, Sept. 15
34°N, 118°W, June 21

Ozone Concentration Transported Aloft

0 ppb
40 ppb
120 ppb
200 ppb

Initial Concentrations***

1.2/0.2	1.76/0.11
0.24/0.04	0.32/0.02

*Simulations were conducted for all combinations shown. Simulations were conducted only for dilution rate = 13%/hr. Otherwise conditions were given in Table 5.1 except where noted on this figure.

**Emission rates are normalized relative to emissions prior to 8 a.m.

***Each pair represents a simulation using the respective initial NMHC (in ppmC)/NO_x (in ppm).

the various combinations of ozone concentration transported aloft, dilution rate and initial concentrations. These results may be examined to consider both the average impact of transported ozone and the variability of this impact as a function of various parameters. As might be expected, the most significant parameter is the transported ozone concentration itself. As shown in Table 5.5, for ozone concentrations transported aloft of 40 ppb, 120 ppb and 200 ppb, the average increases in peak ozone concentration constitute 40 percent, 48 percent and 45 percent of the respective ozone concentrations aloft. These results suggest that the impact of ozone transport tends to increase in proportion to increases in the transported ozone concentration. The impact of ozone transport also seems to increase roughly in proportion to increases in the transported ozone concentration for any of the various combinations of peak ozone level, NMHC/NO_x ratio and dilution rate shown on Table 5.5.

In addition to looking at average impacts, it is also illuminating to compare the impact of transported ozone on peak ozone concentrations to the transported ozone concentration for individual simulations. The most extreme of such comparisons is an impact of 21 ppb vs. the transport of 120 ppb (18 percent) and an impact of 85 ppb versus the transport of 120 ppb (71 percent), although more extreme values may occasionally occur. It is clear that the entrainment of ozone transported aloft does not cause a simple addition to ozone concentrations in the air parcel. (Table 5.3 suggests that the transport of precursors also does not cause any simple addition, either to precursor concentrations or to ozone concentrations). On the other hand, transported ozone clearly has at least some effect on the chemical processes that produce ozone.

TABLE 5.5 Impact of Ozone Transported Aloft

$NMHC/NO_x$	Base Case Peak Ozone (no transport)	O_3 Concentration Aloft:	Increase in Peak Ozone Attributable to Ozone Transport					
			40 ppb		120 ppb		200 ppb	
		Dilution Rate:	13%/hr	29%/hr	13%/hr	29%/hr	13%/hr	29%/hr
6	328		13 ppb	19 ppb	52 ppb	75 ppb	75 ppb	110 ppb
10	332		10	15	35	55	55	85
16	321		8	12	21	33	NA*	67
6	208		14	22	54	78	80	118
10	208		13	18	47	64	70	101
16	108		18	24	66	85	95	129
6	108		18	24	66	85	95	129
10	100		17	22	62	77	90	122
16	102		15	20	59	75	85	118
		Average	16 ppb		57 ppb		91 ppb	
		% of O_3 Aloft	40%		48%		45%	

*NA - Not Available

Table 5.5 may also be used to examine the impact of transported ozone as a function of the peak ozone level, NMHC/NO_x ratio and dilution rate. The first of these variables, peak ozone concentration, represents the maximum ozone levels with no transport of pollutants into the city. This may be considered an indicator of the quantity and concentration of locally emitted precursors. For any given NMHC/NO_x ratio and dilution rate, the impact of pollutant transport increases as the concentration of locally emitted precursors decreases. This is an expected result. As a second result, for each peak ozone level and dilution rate, a decrease in the NMHC/NO_x ratio can cause a substantial increase in the impact of transport. This suggests the importance of the chemical interaction of the transported ozone and the precursor emissions. If an air parcel with a low NMHC/NO_x ratio is assumed unable to produce a high NO_2/NO_x ratio, the role of transported ozone may be to foster the high NO_2/NO_x ratio needed to produce high ozone concentrations. As a third result, an increase in the hourly dilution rate can be seen to cause an increase in the impact of ozone transport. This is an expected result, since a greater hourly dilution, i.e., a more rapid increase in the mixing height, means more rapid entrainment of the ozone aloft.

Simulations were also conducted to investigate variations of the impact of ozone transport under differing conditions of relative emission rates and light intensity. Relative emission rates seem to be most critically affected by the assumptions regarding location of the air parcel relative to the city. Among the assumptions made in the base set of simulations are that the air parcel being modeled stayed in the center of the city until 9 a.m. LDT and then left the city three hours later. Relative emission rates were also derived using two other assumptions: (1) the air parcel stagnated at the

center of the city for the entire day, and (2) the air parcel moved steadily across the city, reaching the center of the city at 7:30 a.m. LDT and leaving the city three hours later. Figure 5.3 shows the relative emission rates derived using the base set of assumptions and the rates derived using these two alternate assumptions. This figure shows that the use of an assumption of stagnation conditions results in a greater fraction of emissions entering the air parcel later in the day. These simulations should represent a typical range of temporal patterns of relative emission rates.

The peak ozone concentrations in the absence of ozone transport and with the impact of ozone transport under these several assumed emissions conditions, are shown in Table 5.6. The peak ozone concentration without ozone transport obviously increases and decreases as the total amount of precursors injected into the system increases and decreases. In this regard, it is interesting to note that the peak ozone concentration is distinctly non-linear with the total precursor emissions. Instead, a better hypothesis is that the peak ozone concentration is mostly affected by emissions occurring prior to midmorning.

It is clear that the impact of ozone transport is noticeably reduced if emissions into the air parcel occur later in the day, and it is almost always slightly increased if emissions occur earlier. Thus, it appears that if any change occurs that results in a greater fraction of the emissions into the air parcel occurring later, e.g., a slowing of the wind or shifting the emissions out away from the center of the city or to later in the day, the impact of ozone transport will generally decrease.

The results of the simulations using alternative diurnal distributions of light intensity are shown in Table 5.7. As stated earlier, the alternative

TABLE 5.6 Impact of Ozone Transported Aloft Under Different Emission Conditions

Emissions Conditions	NMHC (ppmC)/NO_x (ppm)	Peak O_3 Without Transport	Increase in the Peak Ozone Concentration Caused by the Transport of: 40 ppb O_3	120 ppb O_3	200 ppb O_3
Emissions Throughout Day (Stagnation)	1.2/0.2	370 ppb	11	30	51
	1.76/0.11	335	6	18	36
	0.24/0.04	134	16	53	81
	0.32/0.02	127	13	43	61
Emissions Early in Day (Persistent Winds)	1.2/0.2	300	14	56	80
	1.76/0.11	302	7	23	23
	0.24/0.04	97	18	70	98
	0.32/0.02	92	16	62	90
Base Case (Persistent Winds after 9 a.m)	1.2/0.2	328	13	52	75
	1.76/0.11	321	8	21	--*
	0.24/0.04	108	18	66	95
	0.32/0.02	102	15	59	85

*Value missing

TABLE 5.7 Impact of Ozone Transported Aloft Under Different Insolation Assumptions

Insolation Conditions	NMHC (ppmC)/NO_x (ppm)	Peak O_3 Without Transport	Increase in the Peak Ozone Concentration Caused by the Transport of: 40 ppb O_3	120 ppb O_3	200 ppb O_3
34°N, 118°W, June 21	1.2/0.2	362	4	49	70
	1.76/0.11	346	7	26	41
	0.24/0.04	117	19	63	85
	0.32/0.02	112	14	56	80
Base Case (40°N, 75°W,) Sept. 15	1.2/0.2	328	13	52	75
	1.76/0.11	321	8	21	NA*
	0.24/0.04	108	18	66	95
	0.32/0.02	102	15	59	85

*NA - Not Available

insolation distribution has a peak light intensity roughly 17 percent higher and an integrated average light intensity roughly 10 percent higher than the base case insolation. Table 5.7 shows that, in these cases, the peak ozone concentration increases with increased light intensity. However, the increase is generally less than 10 percent and is not readily quantified in terms of the increase in light intensity.

It is interesting to observe from Table 5.7 that, if the light intensity is increased, the impact of ozone transport is generally slightly less. Although there is insufficient evidence to support any single explanation of this effect, this again suggests the importance of the interaction of transported ozone with the photochemical reactions occurring in the primary air parcel. However, variations within the normal range of insolation during the part of the year when high ozone concentrations generally occur would have little effect on the impact of ozone transport.

Table 5.8 summarizes the results discussed in this section. This table lists the variables discussed previously, in approximate order of the sensitivity of the impact of ozone transport within the typical range of values of these variables. For more quantitative results, it is necessary to refer to Tables 5.5, 5.6, and 5.7.

5.6 Anticipated Trends in the Impact of Ozone Transport

The findings discussed in the previous section are the result of simulations that consider a typical range of current conditions. That is, these simulations represent conditions in which the peak ozone concentration in the urban area is still above the NAAQS, and the transported ozone concentration aloft is in some cases significantly above natural background levels. This

TABLE 5.8

The Impact of Ozone Transport Under Varying Conditions--Summary of Results

Variable	Change in Variable	Change in Impact of Ozone Transport
Transported Ozone	Increase	Increase
Dilution Rate	Increase	Increase
Peak Ozone Concentration	Decrease	Increase
NMHC/NO_x Ratio	Decrease	Increase
Emissions Into the Air Parcel	A Higher Proportion Occurring Earlier (e.g., more persistent winds)	Increase
Light Intensity	Decrease	Slight Increase

section is intended to consider the impact of ozone transport under conditions that are likely to exist when the NAAQS is approached.

In making projections for days in which high ozone concentrations occur in the future, it is generally assumed that the future and current meteorological conditions for those days will be similar. However, the future impact of pollutant transport may be significantly affected by reductions in local emissions and, in many cases, by reductions in the transported pollutant concentrations resulting from control programs in upwind areas. The reductions in emissions will generally involve a greater reduction in hydrocarbon emissions than in NO_x emissions. Therefore, future NMHC/NO_x ratios will probably be lower than current ratios. In those cases where transported pollutant concentrations are currently in excess of natural background concentrations, it is reasonable to assume that, as upwind emission control programs take effect, transported pollutant concentrations will be reduced to levels approaching natural background concentrations.

In order to assess the future impact of ozone transport, simulations were conducted with two different NMHC/NO_x ratios that might be expected to occur in the future, the two dilution rates used previously, and appropriate initial concentrations such that the peak ozone concentration in the presence of ozone transport was about 0.08 ppm. These simulations all used the base case conditions of this study for insolation, relative emission rates and initial NO_2/NO_x relationship (i.e., those conditions shown in Table 5.1).

The 8 a.m. NMHC and NO_x concentrations that were simulated and the impact of transport under these conditions are shown in Table 5.9. In each case, the impact of ozone transport indicates the difference between the peak ozone

TABLE 5.9

The Impact of Ozone Transport as Air Quality Approaches the NAAQS

Conditions Simulated

NMHC/NO_x	dilution rate 13%/hr.	29%/hr.
2.5	0.125/0.05	0.3/0.12
4	0.10/0.025	0.2/0.05

This table shows the initial NMHC (in ppmC)/NO_x (in ppm) used in each simulation. All simulations were based on relative emission rates, insolation, and the NO_2/NO_x relationships given in Table 5.1 All simulations were conducted with and without the transport of 0.04 ppm O_3, and all simulations in the presence of ozone transport produced a peak ozone concentration of about 0.08 ppm.

The Increase in Peak Ozone Concentration Due to Consideration of Ozone Transport

NMHC/NO_x	Impact of transport of 40 ppb O_3 Dilution rate = 13%/hr.	Dilution rate = 29%/hr.
2.5:1	31 ppb	28 ppb
4:1	21 ppb	25 ppb

concentration in the presence of transport of 40 ppb ozone and the peak ozone concentration in the absence of transport. The information in this table is in many ways merely an extension and a confirmation of the trends suggested by the simulations of current conditions. The future impact of ozone transport will in many cases be lessened simply because the transported ozone concentration is less. However, if a comparison is made of the current and future impacts of the transport of 40 ppb ozone, the future impact would be expected to be greater than the current impact, due both to the generally reduced emission levels of the city and to the reduced NMHC/NO_x ratio. In addition, Table 5.9 provides further evidence that the impact of the transport of a given ozone concentration generally increases as the NMHC/NO_x ratio decreases, although the evidence regarding variations in the impact of ozone transport with various dilution rates is somewhat ambiguous.

5.7 Conclusions

This discussion presents the results of a study using the kinetics model underlying EKMA to estimate the impact of pollutant transport on the peak ozone concentrations occurring in an urban area. The study was divided into two parts: (1) analyzing the impact of the transport of various pollutants in the surface layer and aloft, and (2) analyzing the impact of transported ozone under various conditions. In the first part of this study, the transport of ozone into a city was found to have a greater effect on the city's peak ozone concentration than did the transport of other pollutants. The dominant cause of the impact of ozone transport was found to be the ozone transported in a layer aloft. The second part of this study assessed the changes in the impact of ozone transport occurring with varying peak ozone levels, dilution rates, NMHC/NO_x ratios, relative emission rates and diurnal light intensity distributions.

Most of these simulations were directed toward estimating the impact of ozone transport under a range of current conditions. These findings were used, together with some additional simulations, to estimate the probable impact of ozone transport as the NAAQS for oxidants is approached.

As discussed previously, one of the assumptions inherent in a kinetics model is that instantaneous vertical mixing occurs. The mixing of ground level emissions and pollutants entrained from aloft were therefore simulated as occurring more rapidly than is actually the case. This may be compared with the treatment of vertical mixing found in most photochemical dispersion models, whereby a column of air is divided into several layers and a finite diffusivity and vertical flow are used to account for pollutant transfer between layers. This study was based on the assumption that ambient vertical mixing within the surface layer is rapid enough that a kinetics model can be used to compare the impact of transport of various pollutants and to estimate the sensitivity of the impact of pollutant transport for various conditions. A clear need exists to assess further some of the findings of this study by using a photochemical dispersion model.

Nevertheless, in spite of the limitations of this study, the results support several conclusions. The first set of conclusions results from the comparison of the relative impacts of various transported pollutants. Unless another city is located immediately upwind, transport of ozone, particularly ozone transported aloft, will almost certainly have a greater impact on an urban area's peak ozone concentration than the transport of any other pollutant. Thus, it is generally more important to obtain accurate measurements of transported ozone than of other transported pollutants. However, the

chemical interactions of this transported ozone with the urban emissions are such that the impact is generally much less than if the transported ozone were simply added like an inert pollutant. The second set of conclusions results from the analysis of the variations of the impact of ozone transport under various conditions. This study also suggests that for a given transported ozone concentration, the absolute impact of ozone transport can be expected to increase as the local emissions of precursors decrease and as the NMHC/NO_x ratio decreases. However, this increase in the impact of ozone transport may well be overwhelmed by the effect of reductions in the transported ozone concentration, as emission control programs in upwind areas take effect. Due to the assumptions used in the model and in the derivation of the input data, it may be inappropriate to use the quantitative results in this study to estimate the impact of transport in individual cities. However, if specific data are available for an individual city, the techniques described herein might be used to estimate the impact of transport on peak ozone concentrations. In any case, the results of this study clearly demonstrate that ozone transported into a city in a layer aloft can, in a wide variety of situations, have a significant effect on that city's peak ozone concentration.

5.8 References

1. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors, EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

2. M. C. Dodge, "Combined Use of Modeling Techniques and Smog Chamber Data to Derive Ozone-Precursor Relationships," International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings: Volume II, EPA-600/3-77-001b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977, p. 881.

3. G. Z. Whitten and H. Hogo, User's Manual for a Kinetics Model and Ozone Isopleth Plotting Package, Draft Final Report, Systems Applications, Inc., San Rafael, California, November 1977.

4. L. H. Titlemore, et al., An Analysis of Urban Area Travel by Time of Day, FH-11-7519, Federal Highway Administration, Washington, D. C., January 1972.

5. B. Dimitriades, ed., International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings: Volume I, EPA-600/3-77-001a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977, pp. 227-338.

6.0 ACKNOWLEDGEMENTS

This document was prepared by the following members of the staff of the Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency: Warren P. Freas, John E. Summerhays, Emerico L. Martinez, Edwin L. Meyer, Jr., Norman C. Possiel and Donald H. Sennett. Whitmel M. Joyner provided editorial assistance, and Mrs. Carole Mask prepared the manuscript. In addition, numerous studies conducted in-house or under contract to the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, were of great assistance in preparing this document.